SYNTHESIS AND CHARACTERIZATION OF NEW POLYBENZOXAZINE BISPHENOL-S BASED TERPOLYMERS FOR TOXIC METAL ION REMOVAL FROM WASTEWATER

BY

Mohamad Estaitie

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Dedication

I dedicate this work to my family, friends, and my teammate Ahmad Alloush

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I cannot express my gratitude towards the people who supported me during my MS degree at KFUPM. First off, my sincere obligation goes to my family members specially my mother and father.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

ABSTRACT

Full Name : [Mohamad Estaitie]

Thesis Title : [SYNTHESIS AND CHARACTERIZATION OF NEW POLYBENZOXAZINE BISPHENOL-S BASED TERPOLYMERS FOR TOXIC METAL ION REMOVAL FROM WASTEWATER]

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A polymeric series were synthesized via Mannich polycondensation protocol utilizing several diaminoalkanes, paraformaldehyde, and Bisphenol-S/pyrrole. The synthetic steps of the terpolymers were optimized under various conditions including temperature and the type of solvent used to obtain high molecular mass. Characterization experiments of the newly synthesized polymers were conducting by using NMR spectroscopy, Fourier Transform Infrared Spectroscopy (FT-IR) and C H N S analyzer. Thermogravimetric Analysis (TGA) were performed to study the thermal properties of the new polymers. X-ray Diffraction (XRD) was used to observe the crystallinity behavior of the synthesized terpolymers.

The new polymers were evaluated for their effectiveness in the removal of toxic metal ions (lead and arsenic) by adsorption under various optimized conditions (pH, contact time, initial metal ion, and concentration). Adsorption of heavy metal from aqueous solutions studies were conducted to evaluate the terpolymers performance. The mechanism of the adsorption of metal ions was studied using various isotherm models such as Langmuir and Freundlich. The synthesized terpolyamine was subjected to chemical modification with carbon disulfide to yield a dithiocarbamate (DTC) functionality. Further

characterization studies were conducted to confirm the presence of DTC functionality before utilizing the new modified polymers in heavy metal adsorption experiments.

ملخص الرسالة

الاسم الكامل: محمد استيتيه

عنوان الرسالة: تصنيع وتوصيف بوليمرات البينزوزاكزين الجديدة المبنية على البيسفينول وتطبيقاتها في تنقية المياه من المعادن السامة

التخصص: كيمياء

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في هذه الدراسة تم تصنيع سلسلة من البوليمرات بطريقة مانيخ للتكثيف باستخدام الكـيـنــات ثنائيـــة الأمين، فورمالهيد وبسفينول-S، ميلامين والبيرول. وتم التركيز دراسة العوامل المؤثرة من اجل للحصول على بوليمرات ذات ثبات عالي ضد الحرارة. لذلك تم تغيير بعض ظروف التفاعل الكيميائي كالحرارة والمذيب وذلك للحصول على أفضل الظروف. تم توصيف البوليمرات الجديدة عن طريق استخدام عدة اجهزة مثل الرنين النووي المغناطيسي وجهاز الأشعة تحت الحمراء لتأكيد ماهية الترابط بين الذرات في البوليمرات. جهاز الحيود السيني تم استخدامه لمعاينة صفات التبلور لدى البوليمرات الجديدة. التحليل الوزني الحراري للمواد استخدم لدراسة الاستقرار الحراري للبوليمرات. خاصية امتزاز المعادن الثقيلة للبوليمرات قد تم دراستها عن طريق أداء تجارب امتزاز للمعدنين الرصاص والكادميوم في ظروف مختلفة من درجة الحرارة والأس الهيدروجيني والتركيز البدائي لمحاليل المعادن الثقيلة. آلية الامتزاز للبوليمرات قد تم دراستها باستخدام متساويات حرارة عديدة مثل لانغمويز وفروندليتش. البوليمرات الجديدة تم تعديلها عن طريق استخدام ثنائي كبريت الكربون لتقديم مجموعة وظيفية جديدة للبوليمرات وتجريبها مجددا في امتزاز المعادن الثقيلة.

CHAPTER 1

INTRODUCTION

The proposed research is fixated on the synthesis of specialized new polymers via Mannich polycondensation reaction protocol of new polymeric series. Bisphenol-S, several alkyldiamines and paraformaldehyde will be mixed to give the corresponding terpolymer. Another polymeric series will be synthesized from mixing pyrrole with alkyldiamines and paraformaldehyde as the linker. The polymeric series will be tested for the removal of toxic metal ions, e.g. lead (II) and cadmium (II), from aqueous solutions and further application in the treatment of wastewater samples. The main focus of this research is to optimize a convenient one-step synthesis of the two series since to be more appealing as an industrial application in wastewater treatment. After the synthesis of the proposed polymeric series is conducted, the polymers will be characterized by various spectroscopic techniques for structural confirmation the structure and surface topography. The efficiency of toxic metal removal of the synthesized polymeric series will be tested in aqueous solutions.

The Adsorption efficiency of the synthesized polyamines will be evaluated under various conditions like effect of pH, the effect of metal ion initial concentration, the effect of contact Time and effect of temperature.

Several types of kinetic and thermodynamic isotherms will be obtained from the metal removal experiments data in order to understand the mechanism of metal ion adsorption on the surface of the polymers.

The final stage in this study will be to test the new polymeric materials in the treatment of wastewater samples that will be collected from different water treatment plants.

The knowledge gained from the proposed research could be integrated with different branches of science and engineering such as chemistry, environmental science, material science and chemical engineering. In addition, it is expected from the study to add several values in different aspects of life, for example, reduction in energy consumption used in the purification of water, recognition of new adsorbents synthesized from efficient materials, easy to be synthesized with specialized functionality. The proposed project will play a significant role in enhancing the quality of the environment and human life.

1.1 Research Problems

Highly efficient adsorbents for the removal of toxic metal ions have attracted large attention in recent years as they are easy to synthesize, cheap and can be designed to be selective for the removal of specific toxic metal ions. The current study aims to design and synthesize new polymeric material that is efficient in the removal of toxic metal ions *via* Mannich polycondensation protocol, the new series will be subjected to a chemical modification in order to improve the removal and selectivity toward toxic heavy metal ions. The synthesized polymers and their modification would represent the first of their kind. The new polymeric material will be characterized and evaluated for their efficacy as new adsorbents that can work under various wastewater conditions and will be subjected to real wastewater samples.

1.2 Literature Review

Despite the fact that ~67% of the earth's surface is covered with water, drinkable freshwater only makes ~2.5% of this ratio. Furthermore, around 70% of the freshwater is locked up as glaciers and icecaps. Hence, the recycling process of the limited freshwater available for human kind is needed while failing to do so may arise health risks. The indiscriminate disposal of heavy metals (like lead, arsenic and mercury, cadmium, …, etc.) into water which is caused by several activities done by mankind, especially industrial, has a potential threat to living systems as these metals are known for their bioaccumulation and non-biodegradable behavior which leads to various diseases and disorders even at trace levels [1-4]. Therefore, Regulation all over the world has been imposed stating that all the heavy metals with toxic properties must be removed or minimized. Recently, the achievement of sustainable and environmentally friendly processes for the removal of such pollutants has become an urgent matter of concern [5, 6].

Several techniques have been used in wastewater treatment. These techniques include ion exchange, flocculation, electrochemical treatment, membrane separation, evaporation, chemical precipitation, reverse osmosis…etc. However, adsorption shows superior performance among the methods in wastewater treatment mentioned above due to its high efficiency and low cost of operation. Many types of adsorbents were tests over the years like polymers, activated charcoal, inorganic materials, graphene and graphene oxides [7-11].

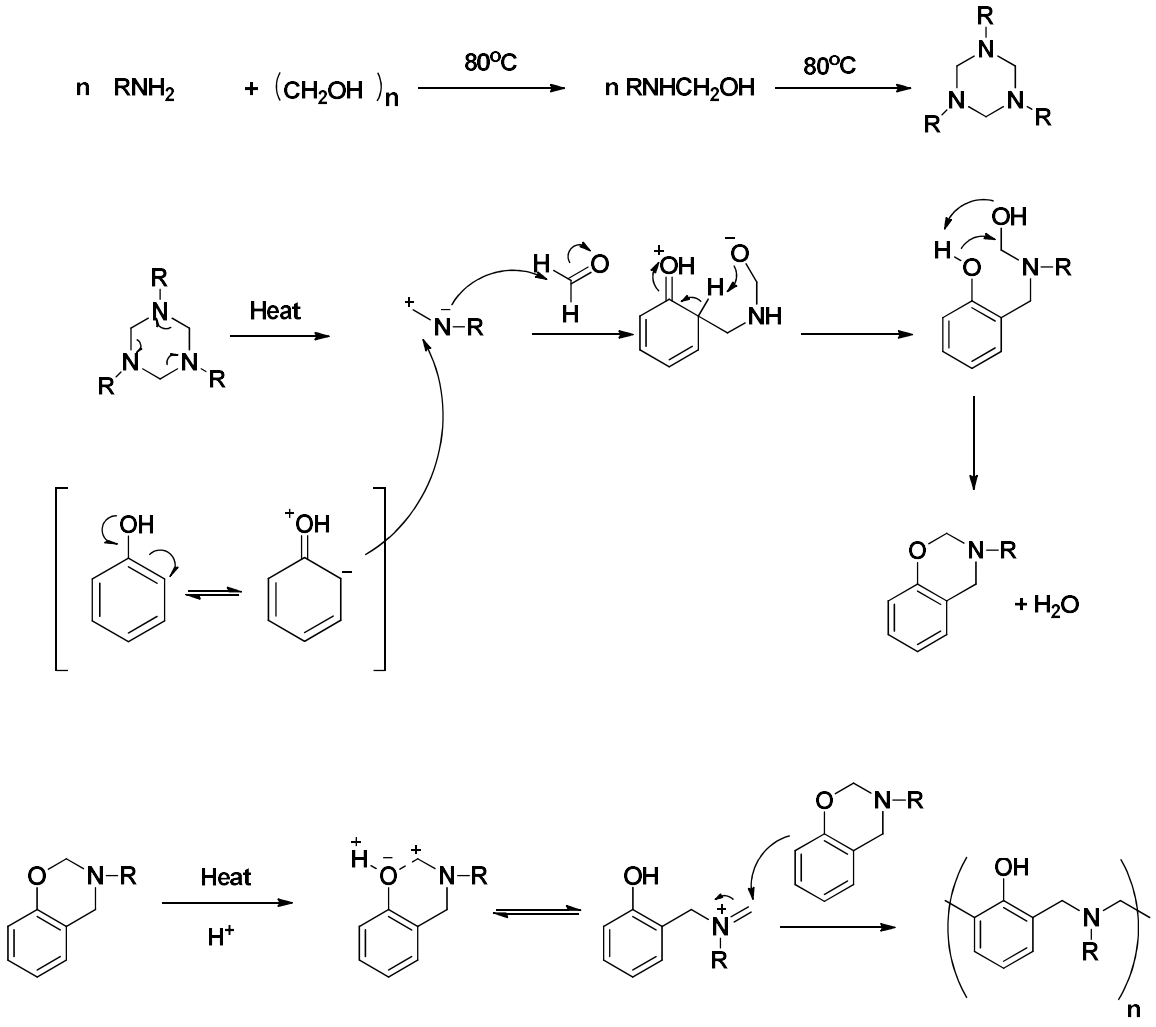
Mannich reaction is a well-known condensation reaction where aminoalkylation occurs for enolizable ketones or aldehydes. Carl Mannich was the first to study this type of reactions and expand the knowledge their chemistry through his research into a based

synthetic technique. Since its discovery, it has been employed in many applications. The pharmaceutical applications are at the main importance of Mannich reactions including synthesis of antibiotics and antineoplastic drugs. However, other applications of Mannich reaction have been recorded such as paints and surface-active agents [12].

In Mannich reaction, an iminium ion is produced through a condensation reaction between an amine functional group with formaldehyde where a water molecule is eliminated. Since the carbon of the ion is electron-deficient, the ion acts as an electrophile for the enolate and the reaction proceeds via C-alkylation at the carbon of the enolate attacking the carbon of the iminium ion [12]. If the alkylation reagent is phenol based the formation of benzoxazine ring which can further undergo ring opening reaction with another benzoxazines according to the mechanism which is illustrated in scheme 1 [13, 14].

Polymerization via Mannich protocol is possible when reagents containing at least two amino groups and two acidic α-CH of the enol. Oie et al have reported linear polymers. In their work, a series of linear polymers were synthesized using 2-Methylresorcinol and 1,3-Benzoxazine by ring opening mechanism to give Mannich-like linkage (-CH_2-NR-CH_2-) [15]. Similar to the planned work, Taskin et al. used bisphenol A, paraformaldehyde, and hexaethylenediamine; a crosslinked polymer was obtained using this method due to the several possible sites of bisphenol A where the C-alkylation can take place [16]. Singru et al. reported the synthesis of a polymer resin using melamine as the amine source and p-cresole with formaldehyde; The polymer was tested for wastewater treatment for the removal of various heavy metals e.g. Pb^{2+}, Cd^{2+}….etc [17]. Baraka and others have reported the synthesis of a novel resin which acts as a chelating agent to various heavy metals by mixing nitrilotriacetic acid (NTA) and melamine using Mannich-type

polycondensation reaction; The resin was tested for heavy metal removal from simulated wastewater [18]. The combination of desired functionalities obtained by using Mannich-type polycondensation reactions has allowed researchers to use such polymers in the various application including wastewater treatment [18, 19].



Scheme 1. Benzoxazine ring formation and opening mechanism.

Several compounds and polymers containing amino groups have been tested in literature as heavy metal removal from wastewater. Yao et al. studied the effect pH on the

Cr^{6+} adsorption properties of a synthesized amphiphilic copolymer containing tertiary amino group [20]. Dong et al. utilized polydopamine in the adsorption of the metals $Cu2^{+}$, Cd^{2+}, Pb^{2+}, Hg^{2+} by grafting polyethylenimine which is abundant with amine groups on the surface of polydopamine and then coated with graphene oxide [21]. In the work of Liu et al., the adsorption of Cu ions was tested using poly(glycidyl methacrylate) functionalized with different aliphatic amines which are ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), and tetraethylenepentamine (TEPA); the DETA-functionalised polymer showed exceptional performance in the adsorption capacity because of the relatively higher amine content [22].

In this work, the efficacy of the removal of lead from simulated and real wastewaters will be explored with a series of new polyamines synthesized in a Mannich-type polycondensation reaction.

1.3 Research Objectives

The main objectives are to:

- Synthesize a new series of polyamines using Mannich polycondensation protocol. Alkyldiamine monomers, namely diaminohexane (DAH), diaminoctane (DAO), diaminodecane (DADec) and diaminododecane (DADod) with formaldehyde will be mixed with bisphenol-S. Further modification on the polymer will take place using carbon disulfide to increase the selectivity towards Hg^{2+}.
- Characterization of the synthesized polymers using various spectroscopic techniques, such as 13C-NMR, FT-IR, surface morphologies will be characterized via FE-SEM. Thermal properties will be studied via thermogravimetric analysis and differential scanning calorimetry.

- Test the efficacy of the synthesized polymers in the removal of toxic metal ions in simulated wastewater and real wastewater samples.
- Compare the obtained resulted with literature in order to evaluate the efficacy of the synthesized polymers.

1.4 Expected Outcomes

The expected outcomes of the proposed research project highlighted as:

1. New and efficient series of polyamines will be developed for toxic metals removal from wastewater.
2. Application of the new polymers in batch mode for toxic metals adsorption
3. Application of the polymers for toxic metals removal from real wastewaters.

CHAPTER 2

Synthesis of Novel Terpolymer Series for the Removal of Lead Ions from Aqueous Solutions

Abstract

Three novel, highly cross-linked polymers containing hydroxyl and amine chelating functional groups (***BSPF***, ***BSDF,*** and ***MPF***) were synthesized polycondensation reaction. The adsorption experiments revealed the efficiency of the synthesized cross-linked polymers in the removal of lead ions from aqueous solutions. The adsorption experiments were done under controlled conditions (pH, Time, the initial concentration of metal ions and Temperature). The adsorption experiments showed BSPF cross-linked polymer to be the most efficient polymer for the removal of lead ions in aqueous solution. Treatment of an industrial wastewater sample revealed that ***BSPF*** cross-linked polymer had a removal efficiency ~99% of lead ions showing the excellent efficacy of the synthesized cross-linked polymers to remove toxic metal ions.

Keywords: cross-linked polymers; toxic metal removal; adsorption.

2.1 Introduction

The Discharging process of wastewater containing highly toxic and non-biodegradable, heavy metal ions such as Cd^{2+}, Cu^{2+}, Cr^{2+}, Fe^{3+}, $Pb^{2+}$and Hg^{2+} from various industrial processes e.g. Mining, power generation, metal finishing, electronic device manufacturers and tanneries have become an issue due to their potential damage to the human health and the environment. Some of these metals have a carcinogenic effect and they have no nutritional value to the human body. While others, such as Zn^{2+}, are essential for the human body, but it could be harmful if they were taken in excessive concentration. Therefore, Regulation all over the world has been imposed stating that all the heavy metals with toxic properties must be removed or minimized. Recently, the achievement of sustainable and environmentally friendly processes for the removal of such pollutants has become an urgent matter of concern [5, 6, 21, 23]. Even at trace levels, lead as a heavy metal is toxic, non-biodegradable and tends to bio-accumulate in the cells of living systems. Lead toxicity in the human body causes serious damage to organs such as the kidney, reproductive system, liver, nervous system and brain [24, 25]. Drinking water and lead-based paint in old homes are listed as the primary sources of lead poising [26, 27]. As per the World Health Organization (WHO) standard, the maximum contaminant level of lead for drinking water is 0.01 mg/l, and as per the Drinking Water Standards and Health Advisories 2012 Edition, US Environmental Protection Agency, the maximum contaminant level goal of lead for drinking water is zero [28, 29]. However, usually, effluents discharged from various industries contained above this level. To achieve this goal, various technologies have been developed to remove out lead from wastewaters. This includes precipitation, coagulation, reverse osmosis, ion exchange, solvent extraction, flotation, and membrane separation. However, among the various techniques, adsorption

shows superior performance among the methods in wastewater treatment mentioned above due to its high efficiency and low cost of operation [30-32].

Promising chelating agents containing aminomethylphosphonate moiety were tested and found to have attractive properties as exchange resins with ligands for selective metal ion complexation or phosphonic acid groups to extract heavy metal ions from aqueous solutions or from fuel ethanol solutions [33-35]. Singru et al. reported the synthesis of a polymer resin using melamine and *p*-cresol with formaldehyde; The polymer was tested for wastewater treatment for the removal of various heavy metals e.g. Pb^{2+}, Cd^{2+}….*etc*[17]. Amino/polycarboxylic acid functionalized polymeric adsorbents have been reported to have good chelating properties toward heavy metal ions and thus can be used for the treatment of wastewater [36, 37]. Such materials have also been reported for their renewability and recycling, which is a crucial step in increasing the adsorbent practical applicability [38]. For the elimination of lead from water to achieve the maximum contaminant level goal of lead in the drinking water, novel highly efficient materials are still required to be designed. In this work, we report the synthesis of three cross-linked polymers as adsorbents with proper functional groups that play a critical role in the adsorption performance of lead removal from aqueous media.

2.2 Experimental

2.2.1 Materials

Bisphenol-S (4,4'-Sulfonyldiphenol), 1,6-Diaminohexane, piperazine, melamine, paraformaldehyde, dimethylformamide (DMF) were used as received without purification. Solvents and other chemicals used were of analytical grade.

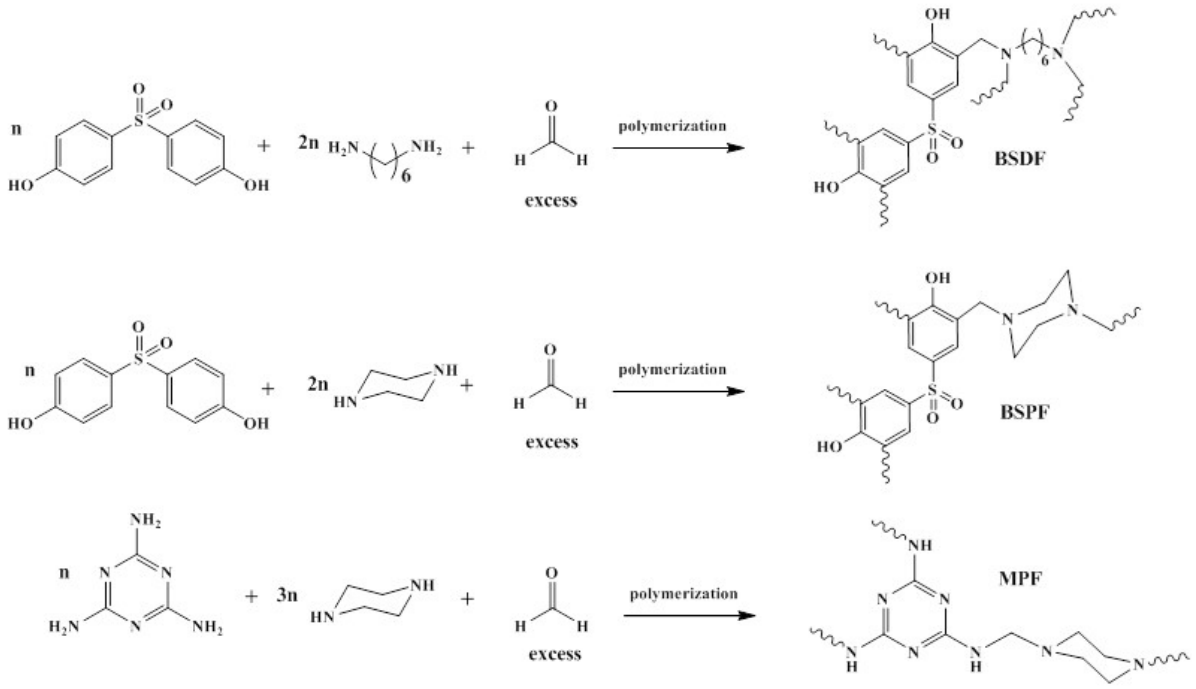
2.2.2 Synthesis of cross-linked polymers

2.2.2.1 Synthesis of Bisphenol-S, paraformaldehyde, 1,6-diaminohexane cross-linked terpolymer (*BSDF*)

A solid mixture of 1,6-diaminohexane (9 mmol, 1.04 g) and paraformaldehyde (22.5 mmol. 0.675g) was dissolved in 10 ml of DMF as a solvent and stirred for 30 minutes. Bisphenol-S (4.5 mmol, 1.11 g) dissolved in 5 ml DMF was added to the mixture and stirred in an oil bath at 140 °C for 24 h. Within 30 min after the temperature was reached 110 °C, the formation of yellow resinous material was observed, which was allowed to stir for 24 hours. The resinous material was washed with water and ethanol several times in order to remove any unreacted material and dried under vacuum at 65 °C until a constant weight is achieved (2.303 g, 83%)(scheme 2). Elementary analysis for ***BSDF***: C (%), 60.0; H (%), 7.36; N (%), 9.35; S (%), 4.62.

2.2.2.2 Synthesis of Bisphenol-S, paraformaldehyde, piperazine cross-linked terpolymer (*BSPF*)

A solid mixture of piperazine (16 mmol, 1.38 g) and paraformaldehyde (33 mmol. 0.962 g) was dissolved 15 ml of DMF as a solvent and stirred for 30 minutes. Bisphenol-S (8 mmol, 2.00 g) dissolved in 15 ml DMF solution was added to the mixture and stirred in an oil bath at 90 °C for 24 h. When the reaction temperature reached 40 °C, the formation of white solid was observed and changed into beige in color after 2 h. For purification purposes, the obtained solid was washed with water and ethanol several timeA solid mixture of piperazine (16 mmol, 1.38 g) and paraformaldehyde (33 mmol. 0.962 g) was dissolved 15 ml of DMF as a solvent and stirred for 30 minutes. Bisphenol-S (8 mmol, 2.00 g) dissolved in 15 ml DMF solution was added to the mixture and stirred in an oil bath at 90 °C for 24 h. When the reaction temperature reached 40 °C, the formation of white solid was observed and changed into beige in color after 2 h. For purification purposes, the obtained solid was washed with water and ethanol several times and dried under vacuum at 65 °C until a constant weight is achieved (3.26 g, 75%)(scheme 2). Elementary analysis for ***BSPF***: C (%), 56.16; H (%), 6.44; N (%), 10.84; S (%), 6.37.



Scheme 2. Synthesis of hyper-cross-linked polymers.

2.2.2.3 Synthesis of melamine, paraformaldehyde, piperazine cross-linked terpolymer (MPF)

A solid mixture of piperazine (30 mmol, 2.58 g), paraformaldehyde (60 mmol. 1.80 g) and melamine (10 mmol, 1.26 g) was dissolved in 25 ml of DMF as a solvent. The solution was stirred at 90 °C for 24 h. A beige colored resinous material was observed after stirring for 5 hours and allowed to stir for 24 hours. The solid product was filtered, washed with acetone and ethanol several times and dried under vacuum at 65 °C until a constant weight is achieved (3.92 g, 77%)(scheme 2). Elementary analysis for ***MPF***: C (%), 46.37; H (%), 7.23; N (%), 34.82; S (%), 0.0.

2.2.3 Adsorption experiments

With a help of computing software, a design of experiment (DOE) was established to examine and evaluate the crucial aspects on the lead removal from wastewater samples and their interactions with at least 95% confidence limit. The DOE is treated to be a more descriptive experimental method than one-variable-at-a-time experimentation. Usually, the latter does not give any information about the interaction between factors in the experiment. For this work, the aspects which affect the adsorption process are defined as follows; polymer type (***BSPF*** = 1, ***MPF*** = 0, ***BSDF*** = -1), pH (3, 5, and 7), the initial concentration of the lead solution (0.2, 2.6 and 5 ppm) and the temperature (298, 318 and 338 K). The choosing of polymer type as a factor is due to the variation of the moieties present in the cross-linked polymers. pH levels of 3, 5 and 7 were chosen due to metal speciation behavior of lead ions at pH > 7 which they can be removed from aqueous solution by the means of precipitation. The simulation of real industrial wastewater samples can be achieved by varying the initial concentration of lead ion solutions. The response variable in this DOE investigation is the percentage removed of lead ions from the solution which is directly related to the removal efficacy of the synthesized polymers under the detailed conditions. The generated data from the DOE experiments are summarized in Table 1.

Table 1. DOE for lead removal experiments and their corresponding percentage removal (%).

Factor				Low level (−1)	High level (+1)
(A) Polymer				-1	+1
(B) pH				3	7
(C) initial concentration of Pb^{2+} (ppm)				0.2	5
(D) Temperature (K)				298	338
Run	(A)	(B)	(C)	(D)	Percentage
1	1	7	0.2	298	99.7
2	-1	3	5.0	298	2.8
3	-1	7	0.2	338	99.6
4	1	3	5.0	338	44.9
5	0	5	2.6	318	31.8
6	-1	3	0.2	298	66.8
7	1	7	5.0	298	33.8
8	1	3	0.2	338	42.0
9	-1	7	5.0	338	54.6
10	0	5	2.6	318	38.2
11	-1	7	0.2	298	99.6
12	1	3	5.0	298	25.5
13	1	7	0.2	338	99.7
14	-1	3	5.0	338	42.0
15	0	5	2.6	318	40.0
16	1	3	0.2	298	96.9
17	-1	7	5.0	298	42.5
18	-1	3	0.2	338	33.7
19	1	7	5.0	338	55.2
20	0	5	2.6	318	39.9

The adsorption of lead ions experiments was conducted as the following method. A stock solution of Pb^{2+} ions was prepared from standard 1000 ppm lead solution and diluted with distilled water. Thereafter, a variety of lead solutions between 0.2 to 5 ppm were prepared from the stock solution. The pH of lead solutions was adjusted by using acetate buffers. The adsorption experiments were performed by batch mode; 20 ml of Pb^{2+} solution of varied concentrations were taken in polyethelene vials and then ~0.03g of the

adsorbent was added in each vial. The suspension was equilibrated by shaking at the fixed desired temperature in a water bath shaker for 6 hours. After equilibration steps occur, the adsorbent was separated from the solution by the means of gravity filtration. The residual Pb^{2+} ions concertation was measured by ICP-MS.

2.3 Results and discussion

BSDF, *BSPF,* and *MPF* cross-linked polymers were produced from Mannich polycondensation reaction. The three cross-linked polymers were found to be insoluble in acidic, basic, polar and nonpolar solvents. The importance of these cross-linked polymers rises from the feasibility of synthesis, characterization, and efficiency in the removal of toxic metal ions from aqueous solutions.

2.3.1 Characterization of cross-linked polymer

FT-IR spectra were recorded on a Perkin Elmer 16F PC FTIR spectrometer and presented in figure 1. For ***BSDF*** and ***BSPF***; The spectra revealed the presence of a broad, strong band at ~3430 cm^{-1} due to –OH & -NH stretching vibrations[13]. The symmetric and asymmetric vibrations of S=O were assigned ~1130 and ~1290 cm^{-1} [39]. The C-N absorption frequency was assigned ~1460 cm^{-1} [40]. ***MPF*** spectra revealed the presence of two bands appears at 3418 & 3469 cm^{-1} arise from the presence of free secondary amines from the melamine moiety in the terpolymer. Aliphatic C-H stretching vibrations from the piperazine rings and the CH_2 linkage were assigned the bands 2877 & 2937 cm^{-1}. The C=N stretching vibrational frequency appears at 1555 cm^{-1}. Aliphatic C-N stretching was assigned the peak 1464 cm^{-1} [40, 41].

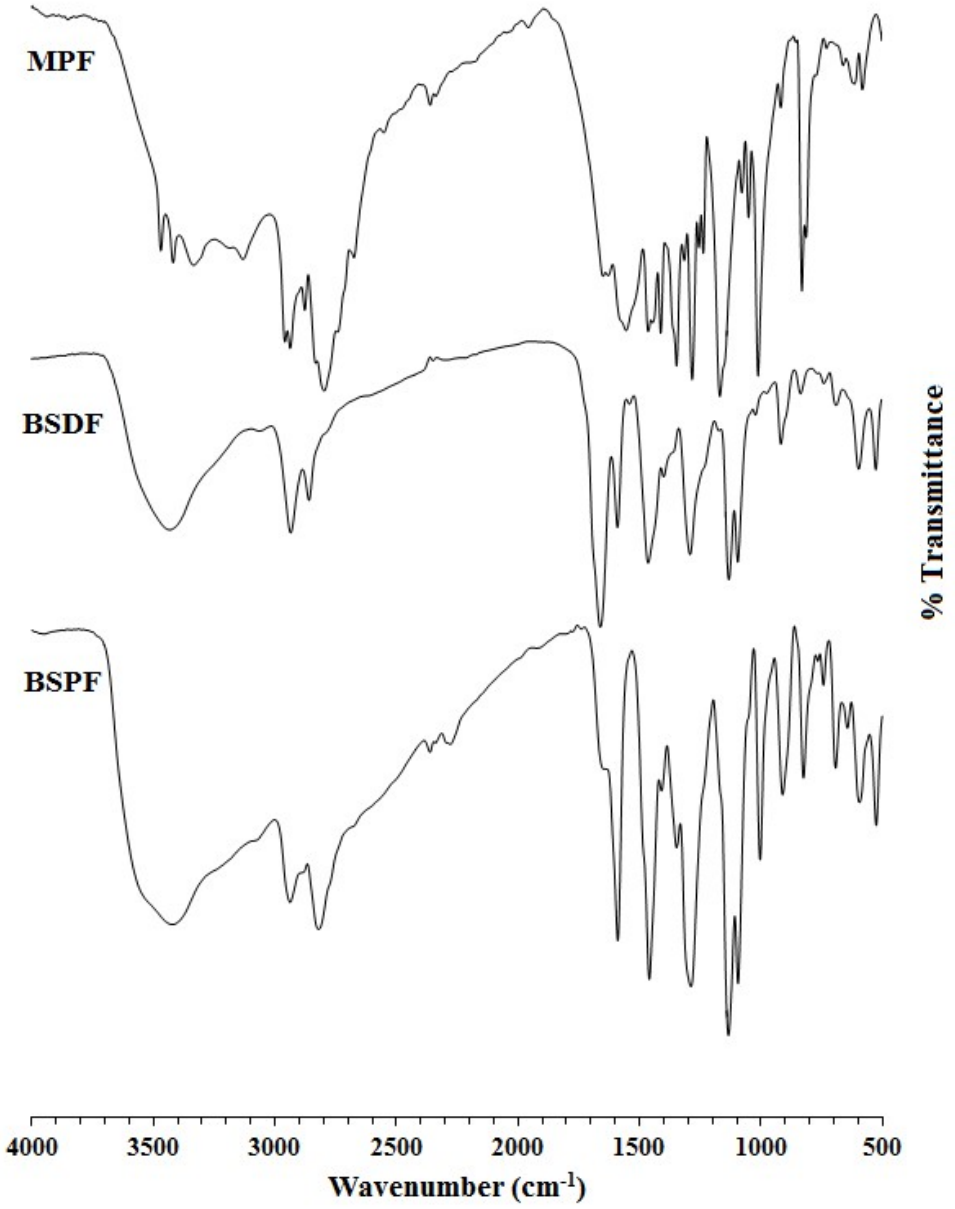


Figure 1. FT-IR spectra of cross-linked polymers.

Solid-state ^{13}C-NMR spectra were taken using Bruker WB-400 spectrometer with a spinning rate of 10 KHz. Solid-state ^{13}C-NMR spectra of the synthesized cross-linked polymers are shown in Figure 2. The assignment of peaks and spectra confirmed the proposed structure shown in the figure, a peak ~80 ppm revealed the formation of a triazine ring in ***MPF***, which was found absent in ***BSDF*** and ***BSPF*** [42-44].

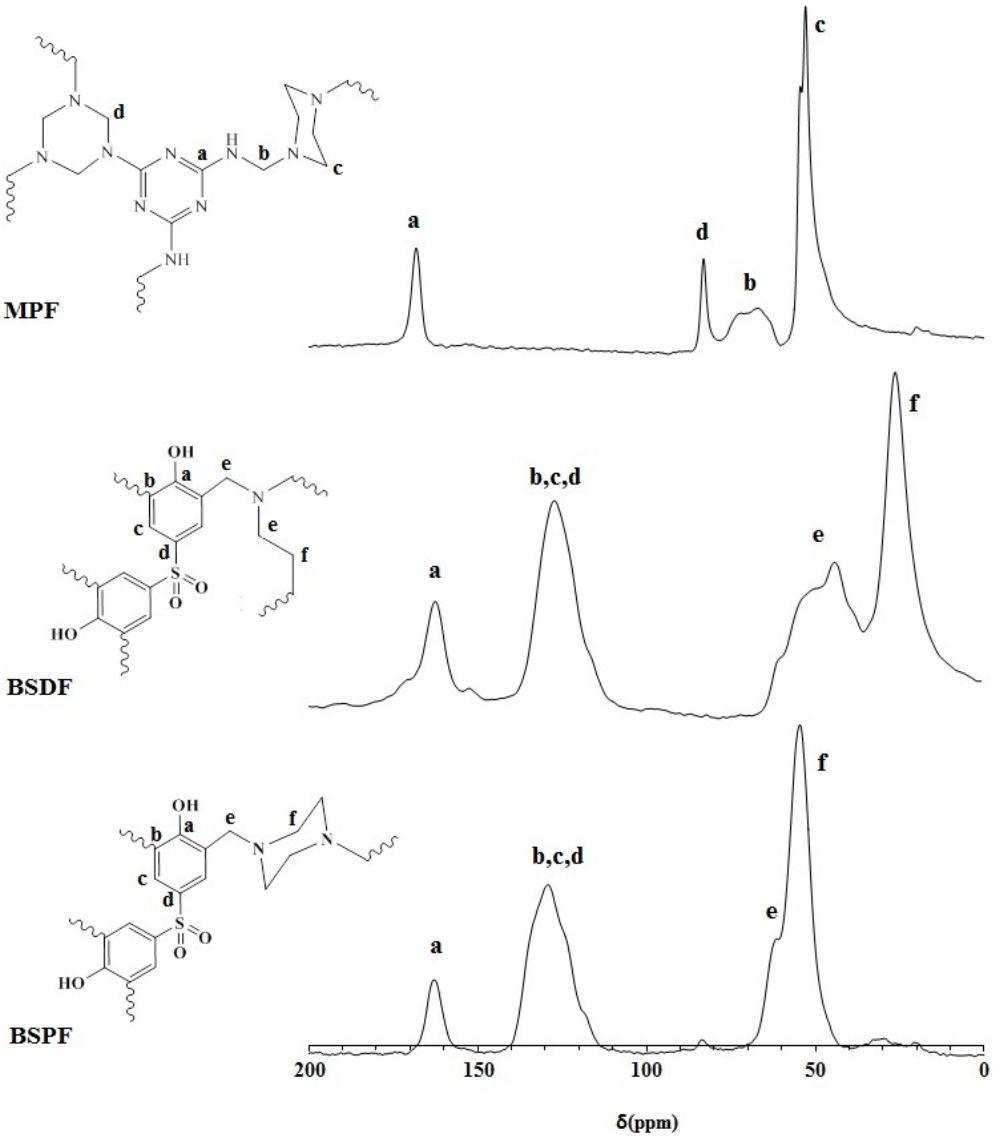


Figure 2. Solid-state ^{13}C-NMR spectra of cross-linked polymers.

Thermal properties of the synthesized cross-linked polymers were investigated by TGA and DSC. Thermogravimetric analysis (TGA) of the synthesized cross-linked polymers shown in figure 3 revealed that ***BSPF*** has the highest thermal stability with thermal degradation starting ~ 250^{o}C whereas ***BSDF*** and ***MPF*** ~180^{o}C. The thermal

stability showed that the presence of the Bisphenol-S moiety increased the thermal stability of the cross-linked polymers.

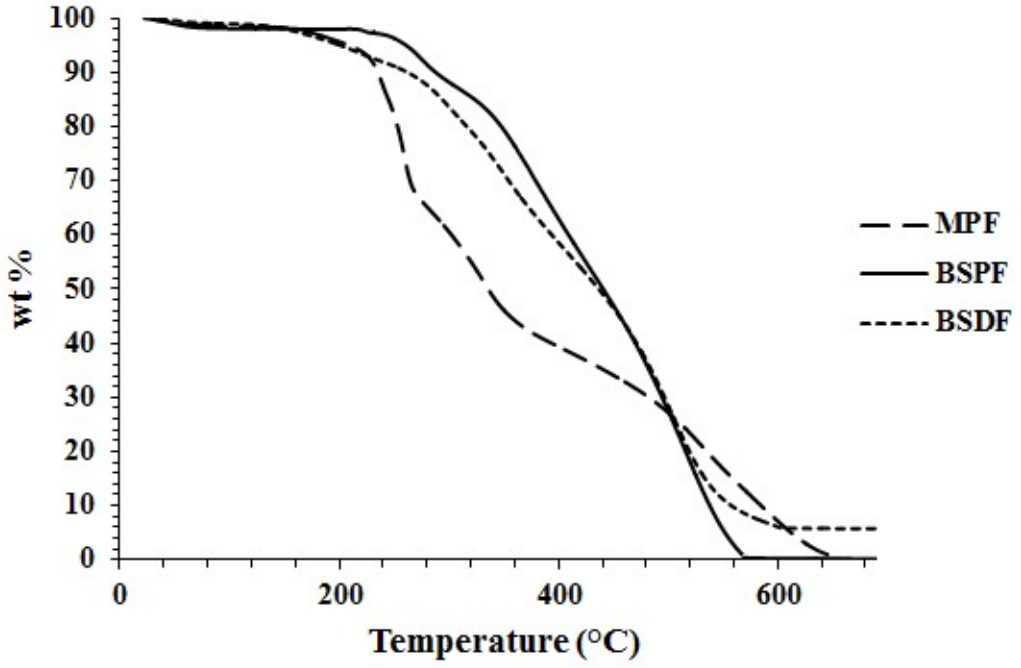


Figure 3. Thermogravimetric Analysis of cross-linked polymers.

Differential scanning calorimetry measurements were performed using NETZSCH DSC 204 F1 Phoenix calorimeter, the thermograms in figure 4 revealed the absence of a glass transition temperature confirming that the material is highly cross-linked in nature. The thermal behavior showed that the cross-linked polymers began to melt ~150ºC followed by decomposition; which could be attributed to the absence of flexible aliphatic fragments, and high concentration of rigid aromatic segments present in the cross-linked polymers [45].

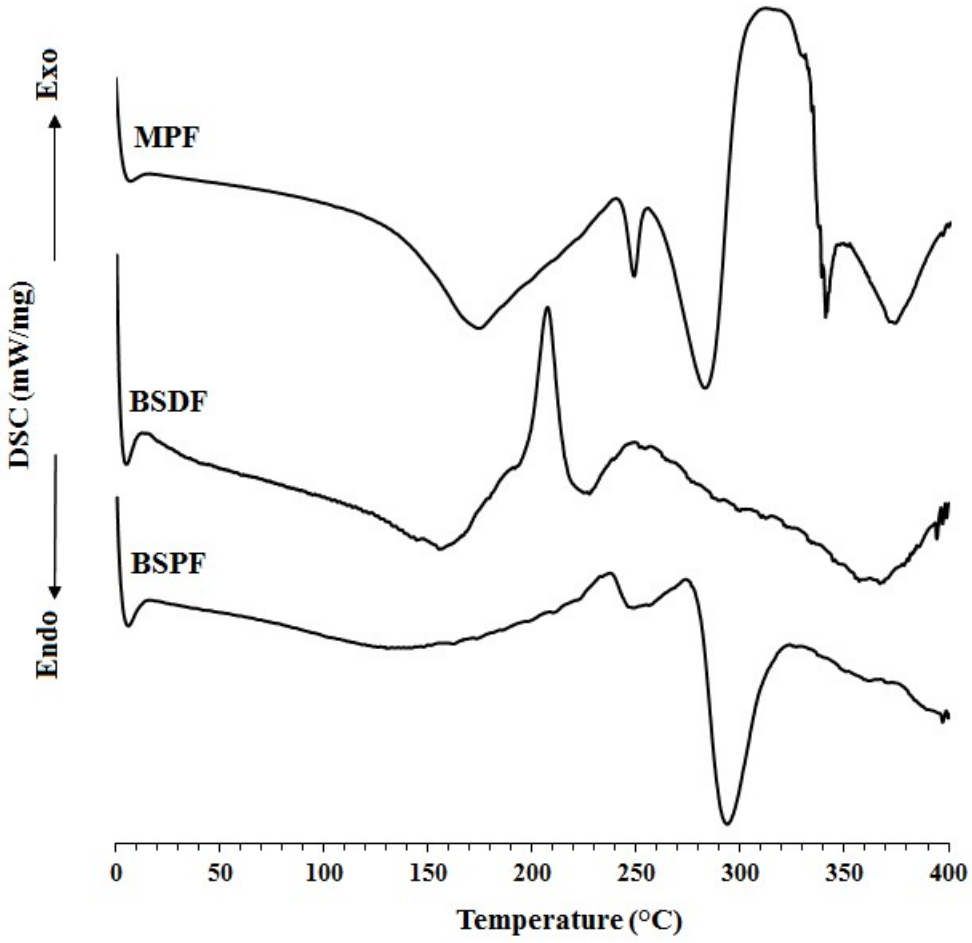


Figure 4. DSC thermograms of the cross-linked polymers.

The surface area of the three cross-linked polymers was analysed utilizing Micrometrics TriStar III BET surface area Analyzer with Burnauer–Emmett–Teller (BET) N_2 method. The analysis revealed that ***BSPF*** cross-linked polymer had the highest surface area (57.6 m^2/g); the adsorption isotherm reveals that ***BSPF*** is mesoporous in nature, whereas, ***BSDF*** (14.3 m^2/g) and ***MPF*** (19.1 m^2/g) are considered to be macroporous in nature. The surface area isotherms provide valuable information as it coincides with the high efficiency of BSPF in the removal of lead ions from aqueous solutions [46].

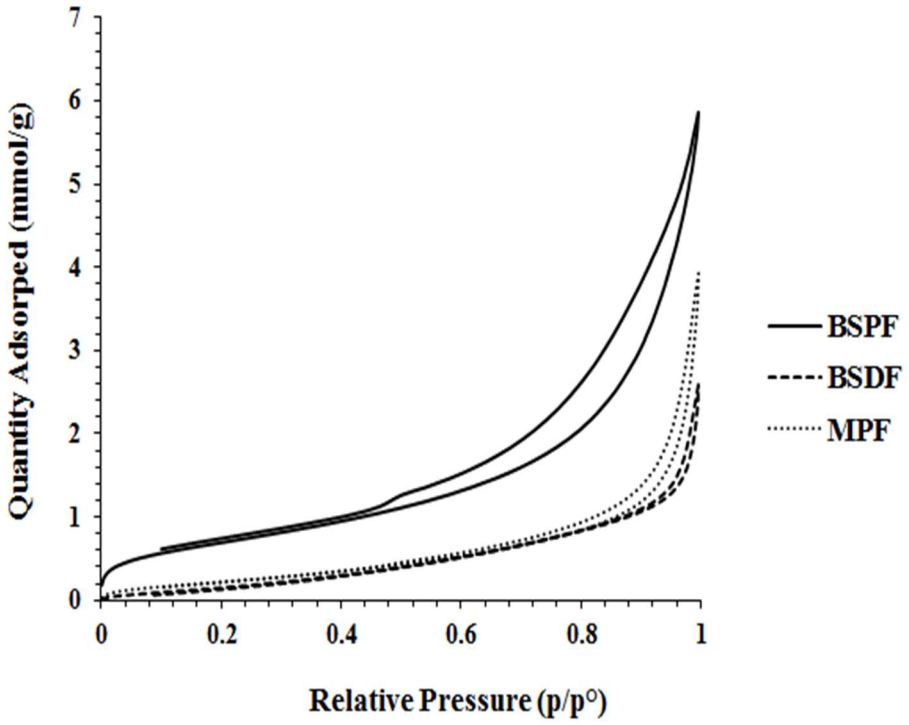


Figure 5. Nitrogen adsorption/desorption isotherms at 77K for ***BSPF***, ***BSDF***, and ***MPF***.

X-ray Diffraction (XRD) patterns shown in figure 6 revealed that ***BSPF*** and ***BSDF*** were Amorphous in nature, whereas ***MPF*** is semicrystalline in nature.

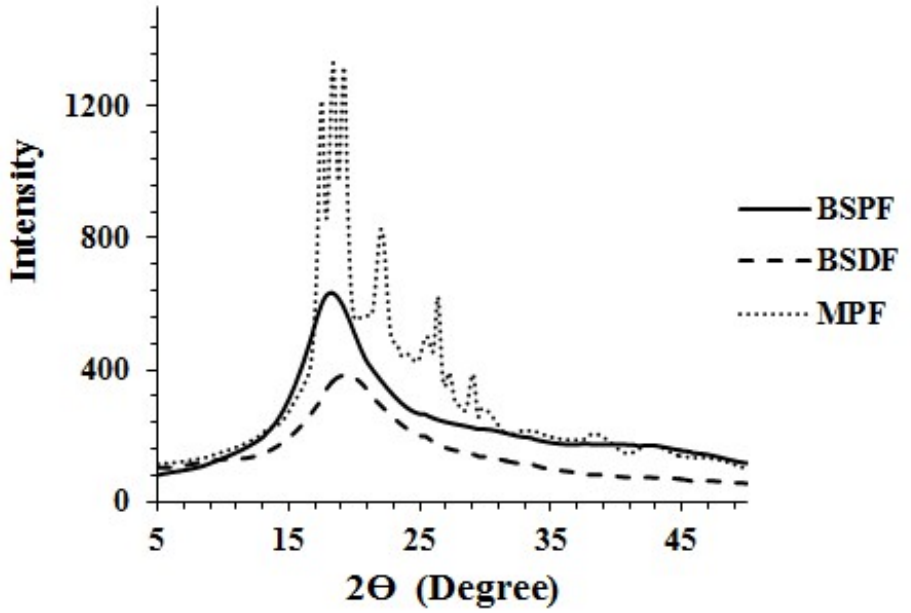


Figure 6. XRD patterns for ***BSPF***, ***BSDF***, and ***MPF***.

2.3.2 Results of the factorial design

Experiments were conducted according to the generated design and % removal of lead under the specified interacted conditions was recorded [40]. Figure 7a-c depict the normal plot, half normal plot and Pareto chart of the standardized effect. The factorial design results show that the initial concentration and pH had the strongest effect on lead removal efficiency. Increasing the pH increases the lead removal. The interaction between initial concentration and the temperature followed by the interaction between pH, initial concentration, and the temperature.

Figure 7a indicates that the polymer ***BSPF*** had the highest adsorption efficiency among the three polymers tested in these experiments. Decreasing the initial concentration increases lead removal efficiency. The interaction between pH and lead initial

concentration had the highest effect on the adsorption, figure 7b. The second highest interaction effect that between polymer type and initial concentration.

Based on the DOE results, the polymer ***BSPF*** was selected to be used in the following work under the obtained optimum conditions. The surface plot in figure 8 indicates the effect of the dosage and temperature on the percentage adsorption of lead by the ***BSPF*** polymer. The plot shows that at polymer has a slightly more affinity toward lead ions at high temperature than ambient conditions. This suggests a superior affinity of ***BSPF*** towards lead ions that can be attributed to high active functionality in the polymer and larger pores.

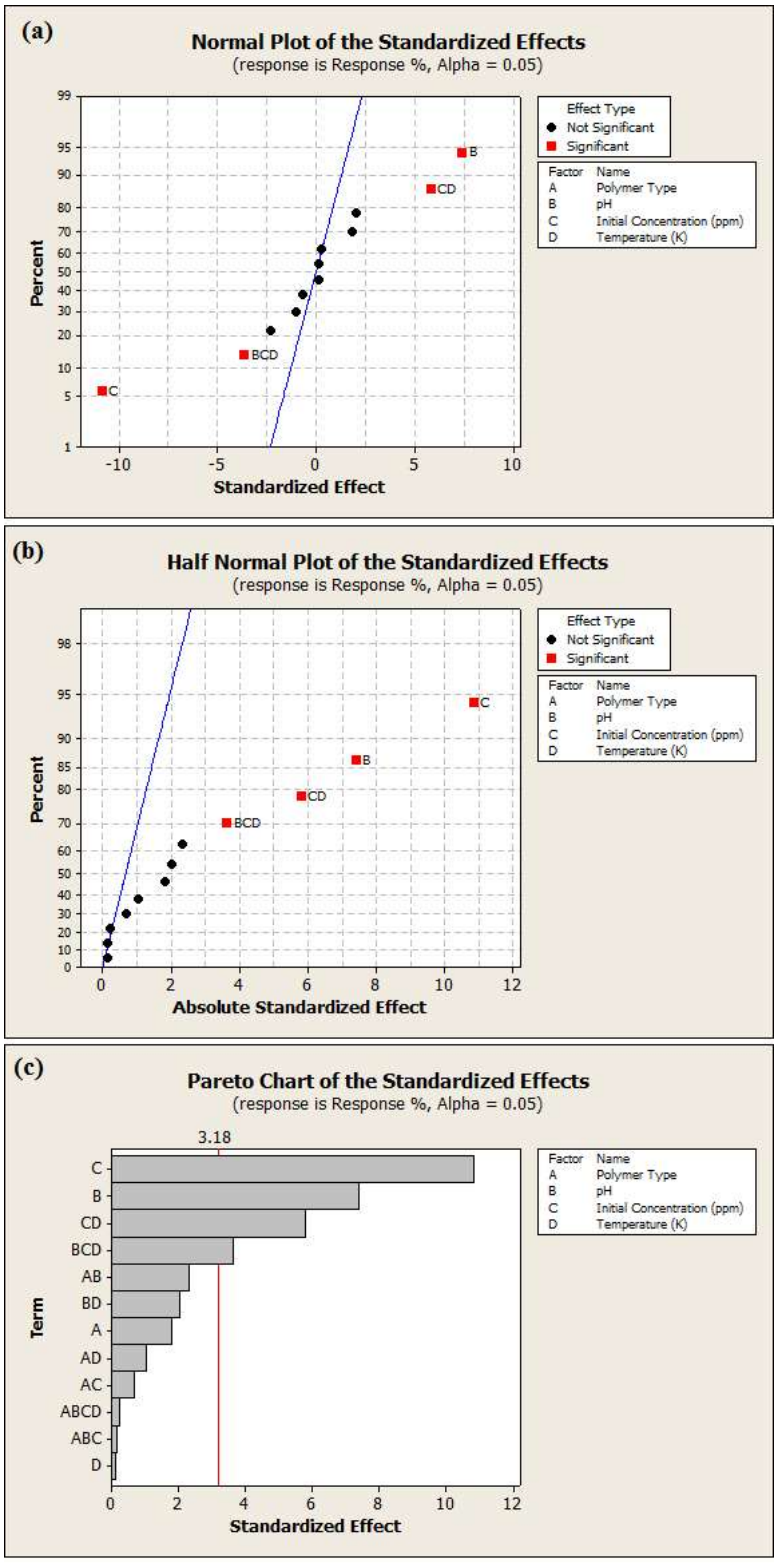


Figure 7. The factorial design plots showing (a) Normal plot (b) half-normal plot and (c) Pareto chart.

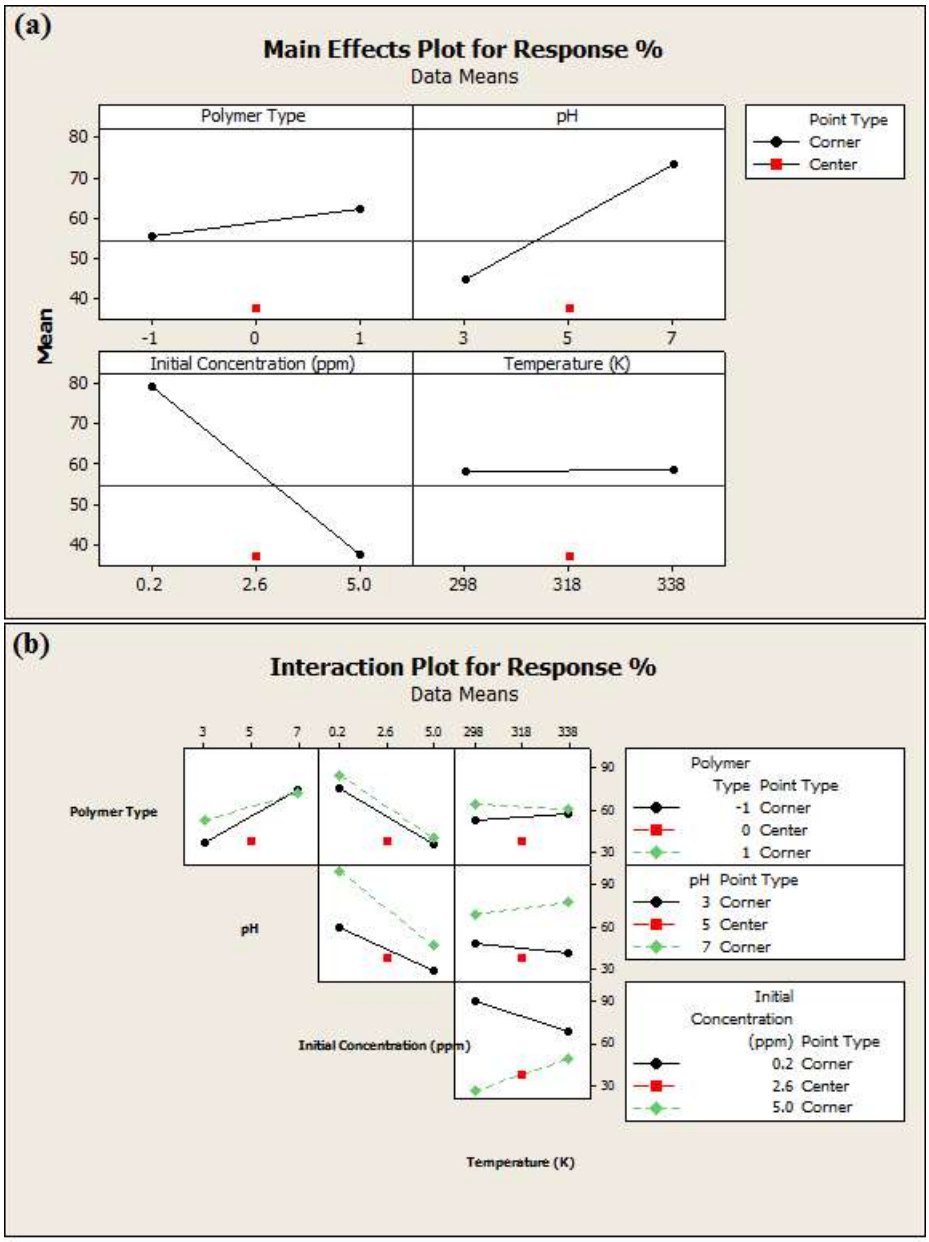


Figure 8. The factorial design plots showing (a) Main effect plot (b) Interaction plot.

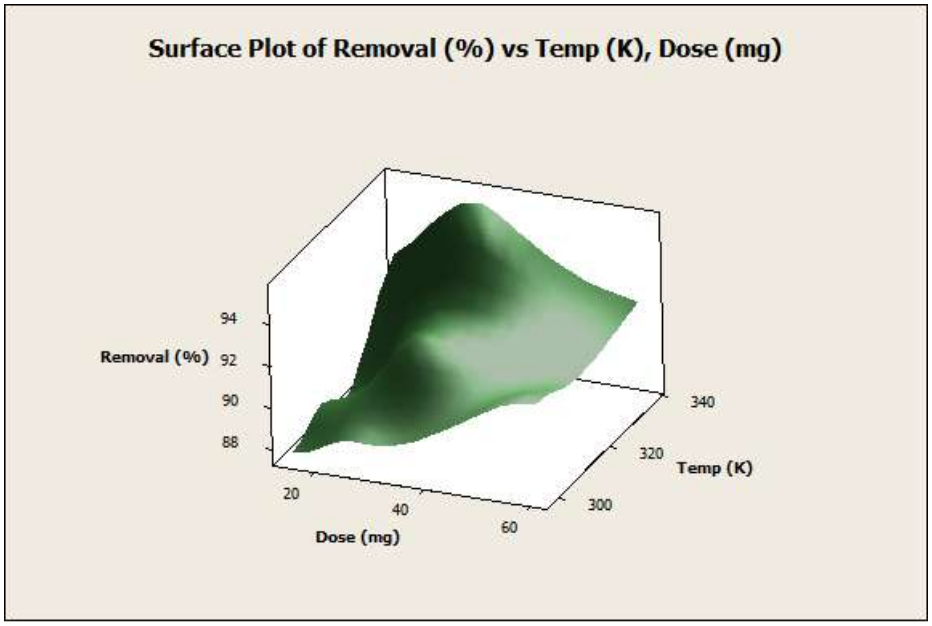


Figure 9. Surface plot of percent removal vs dosage and temperature.

2.4 Wastewater Treatment

In order to evaluate the efficiency of the synthesized cross-linked polymer, BSPF cross-linked polymer was tested on a real wastewater sample spiked with 3 mg/L Lead ions. The results revealed the efficiency of the synthesized cross-linked polymer in the removal of toxic metal ions in real wastewater conditions. ***BSPF*** efficiently removed ~ 99.9% of the spiked lead ions in the waste water sample. The results prove that ***BSPF*** could be utilized as an industrial adsorbent for wastewater treatment.

Table 2. Industrial wastewater spiked with 3 mg/L Lead ions treated with BSPF.

Metal	Before treatmen (µg /L)	After Treatment (µg /L)
Pb (spike	2690 ± 0.438	2.228 ± 0.438
Cd	0.73 ± 0.213	0.711 ± 0.213
As	95.32 ± 7.077	22.78 ± 7.077
Zn	< MDL	< MDL
Cu	20.07± 9.235	25.36 ± 9.235
Ni	39.38 ± 4.275	21.38 ± 4.275
Co	2.504 ± 0.405	1.366 ± 0.405
Mn	6.632 ± 1.215	3.782 ± 1.215
Cr	125.6 ± 3.594	30.81 ± 3.954

Mean and standard deviation of three replicates (n = 3). ± Values a
method detection limit (MDL), 3σ of the blank sample.

2.5 Conclusions

Three novel highly cross-linked polymers (***BSPF***, ***BSDF,*** and ***MPF***) were synthesized via one-pot polycondensation reaction. The synthesized cross-linked polymers were characterized by several techniques, and structure was proven. ***BSPF*** cross-linked polymer showed high efficiency in the removal of lead ions from aqueous solution and proved to be an efficient material for the removal of lead ions (~ 99% removal) in real wastewater sample.

CHAPTER 3

Dithiocarbamate-modified Terpolymers for the Removal of Cadmium Ions from Aqueous Solutions

3.1. Introduction

It is common knowledge that water is essential to living organisms. Hence, any kind of contamination to water resources would raise health risks to humans and other living systems. One of the main contaminants to water resources is heavy metals [47, 48]. Heavy Metals are persistent contaminants which are well-known for their non-biodegradable behavior, bioaccumulation even at trace levels which may cause various of human illness and diseases such as disruption of both endocrine and nervous systems and damages several body organs (e.g. lungs, kidneys, liver, ..., etc.) [49-52]. For that reason, it is crucial to remove these types of pollutants prior to the release of wastewater from industrial process [53].

Cadmium is a heavy metal, which is frequently used in industrial processes including nickel-cadmium batteries, used as an anticorrosive agent and pigments. Albeit cadmium-containing products can be recycled for industrial applications, most cadmium pollution incidents arise from incineration and dumping of cadmium waste [54]. In the recent years, cadmium has had the attention of researchers due to its toxicity behavior which may lead to various diseases such as bone damage, acute respiratory distress

syndromes (ARDS) which arise from inhaling cadmium fumes, and kidney damage [55-57].

Various methods have been implemented in heavy metal removal from wastewater; these methods include precipitation, flocculation, separation using membranes and ion exchange [58, 59]. Among the conventional methods of wastewater treatment, adsorption till now is considered to be the best method for heavy metal removal due to the efficiency of this method and being cost-friendly [60, 61].

The designing process of efficient adsorbent materials is an important criterion for heavy metal removal from wastewater. Hence, many types of materials have been studied for their efficacy in wastewater treatment such as zeolites, biomaterials and activated carbon [62-65]. On the other hand, polymeric materials have shown good performance and remain as one most relevant methods for designing adsorbent materials [66]. The adsorption performance is directly proportional to the functionality of the adsorbent. It has been shown that sulfides [67-69] and other adsorbents containing sulfur moieties such as mercaptobenzothiazoles [70], dithiocarbamates, thiols [71], benzoylthiourea [72], show an excellent performance in the wastewater treatment due to the strong covalent bond which is formed between sulfur and the heavy metal.

For the past few decades, many organic polymers containing sulfur moieties, dithiocarbamate (DTC) moiety is one example of such polymers. Recently, surface modification with DTCs on natural or synthetic composites along with nanoparticles got the attention of researchers for the application in wastewater treatment [73-75]. Several research groups reported the modification of organic polymers with dithiocarbamate functionality. Usually, these polymers are modified through the conversion of a present

primary or secondary amine functionality of the polymer to dithiocarbamate functionality using carbon disuflide [76, 77]. A typical example of the synthesis of dithiocarbamate-modified polymers (DTCP) was reported by the production of DTCP Liu et al. In the reported work, triethylenetetramine was grafted on a co-polymer of dimethyldiallylammonium chloride and acrylamide where the amine moieties were changed into DTC groups [73]. In most cases, the DTCP's could be separated from the reaction mixture of such conversions through precipitation step using acetone [78].

Herein, we report the synthesis of a polymeric series prepared by the reaction between pyrrole and aliphatic diamines where parafolmaldehyde is used as a linker in Mannich-type protocol [79]. The synthesized polymers were subjected to treatment with carbon disulfide to convert the amino group into dithiocarbamates. The modified DTCP's were tested for their efficacy in heavy metal removal from aqueous solutions and wastewater samples.

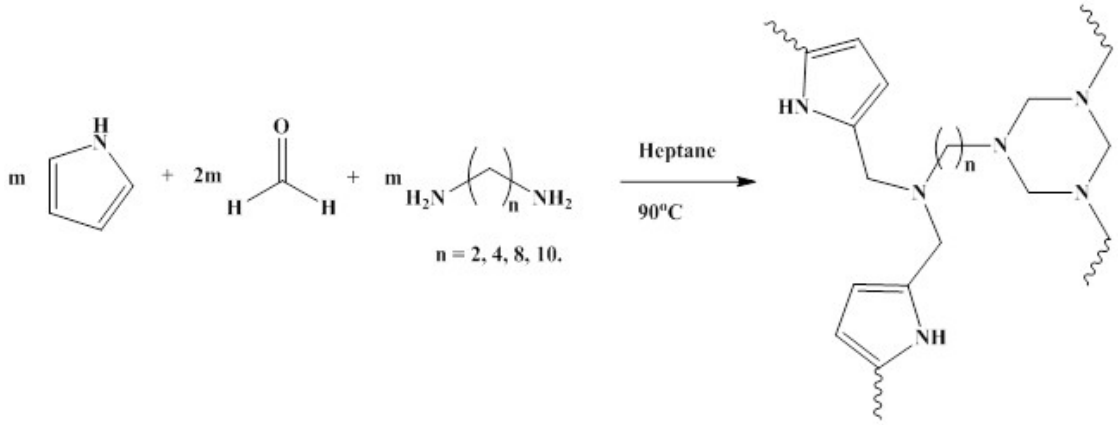
3.2. Experimental

3.2.1 Materials

Pyrrole, 1,2-Diaminoethane, 1,4-Diaminobutane, 1,8-Diamineoctane, 1,10-Diaminodecane, paraformaldehyde, heptane, carbon disulfide, potassium hydroxide, acetone, dimethylformamide (DMF) were used as received without purification. Solvents and other chemicals used were of analytical grade.

3.2.2 Synthesis of the Terpolymers

A mixture of pyrrole (0.01 mol), an alkanediamine (0.01 mol) and paraformaldehyde (0.02 mol) in heptane (20 ml) was stirred at 80°C for 24 h. During the reaction period, the reaction mixture yields the formation of a resinous brownish yellow solid for ethylenediamine and butanediamine and yellowish material for octane- and decanediamine. The solids formed were allowed to cure for 24 hours, the resinous materials were washed with water and acetone several times in order to remove any unreacted material and dried under vacuum at 60°C until constant weight is achieved. The synthetic scheme is shown in (Scheme 3).

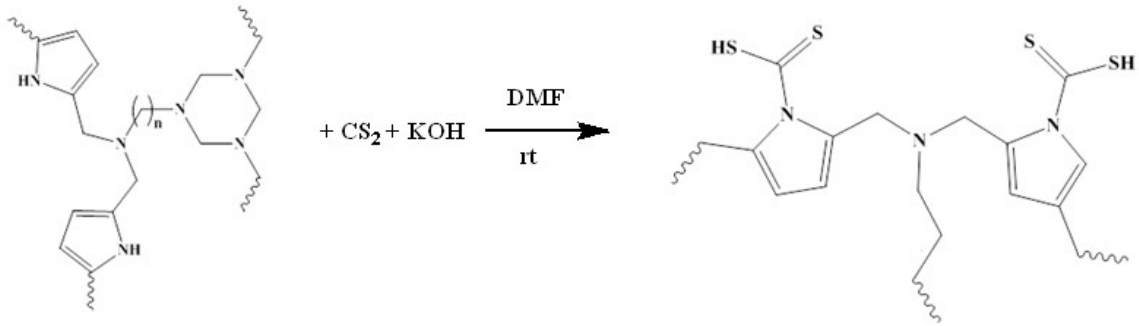


Scheme 3. Synthesis of the terpolymers.

3.2.3 Modification on the Terpolymers

The obtained terpolymers were subjected to modification process through mixing with an excess amount of carbon disulfide (at least 3 equivalents of carbon disulfide per polymeric chain) in the presence of excess potassium hydroxide in DMF. The reaction mixture was stirred for 24 hours at room temperature. The modified polymers were

precipitated from the reaction mixture using acetone and washed with acetone and ethanol several times then dried under vacuum at 60 °C. Scheme 4 shows the modification process on the terpolymers.



Scheme 4. Modification of the Terpolymers with CS_2

3.2.4 Adsorption experiments

Adsorption set of experiments were conducted using the technique of batch equilibrium in polyethylene vials (50 ml capacity). A mixture of 30 mg of the modified polymers immersed in an aqueous solution (20 ml) of Cd^{2+} ions with a concentration of 2 mg L^{-1} to test the effect of the chain length. Once the first adsorption experiment was completed, the best polymer of the series was chosen for further adsorption studies at different concentrations, times, temperatures and pH's. The pH of the solutions was adjusted by preparing acetate buffers. The terpolymers were filtered and the concentration of the metal ions in the filtrate was analyzed. The adsorption capacity of terpolymers was calculated using Eq. (1):

$$q_{Cd^{2+}} = \frac{(C_o - C_e)V}{W} \qquad (1)$$

where C_o is the initial metal ion concentration (mg L^{-1}), C_e is the metal ion concentration at equilibrium (mg L^{-1}), V is the volume of solution (L), W is the weight of the terpolymer (g), and $q_{Cd^{2+}}$ is the adsorption capacity at equilibrium (mg g^{-1}) [66, 80].

3.2.5 Quality control and Quality Assurance

Quality control (QC) was maintained beginning with the design of the experimental work, sampling and continue through the final validation of the obtained results. QC for cadmium ion determinations included repeated of injections and periodic analysis of standard solution. The loss of cadmium and contamination of aliquots were limited to a minimum as per the requirements of quality control and assurance of results. The relative standard deviation of the results was ≤ 5 %.

3.3. Results and Discussions

3.3.1. Synthesis and characterization of cross-linked terpolymers

The results for the polymerization reactions are shown in table 3, elemental analysis of the synthesized cross-linked polymers indicate the successful reaction of pyrrole, formaldehyde as a linker and various alkyldiamines. The cross-linked material synthesized revealed an increase in rubbery like texture as the length of the diamine alkyl chain increased which is considered to be correct as the flexibility of the synthesized cross-linked increases with increasing the length of flexible aliphatic chain from 1,2-ethylenediamine toward 1,10-decanediamine. Elemental analysis shows an increase in the carbon content per repeating unit, and a decrease in the nitrogen content as the ratio of methylene (-CH_2-) units becomes larger and larger with the increase of aliphatic chain of the alkyldiamine.

Table 3. Synthesis results for the cross-linked polymers[a].

Polymer	Yield[b] %	Elemental analysis (%)		
		C	H	N
PY-ED	64	58.21	8.15	24.49
PY-BD	67	60.94	9.11	20.15
PY-OD	82	69.11	10.72	16.07
PY-DD	68	76.47	12.35	15.29

[a] Pyrrole: formaldehyde: diamine= 1:2:1.

[b] Yield = mass of products/mass of reactants *100%.

FT_IR spectra recorded on a Perkin Elmer 16F PC FTIR spectrometer of the synthesized cross-linked polymers are shown in figure 10. Similar characteristic peaks of the synthesized cross-linked polymers reveal of each component are clearly distinguished. It has been observed that the -CH_2- rock peaks around ~720 cm^{-1} is diminishing as the chain becomes shorter and shorter.

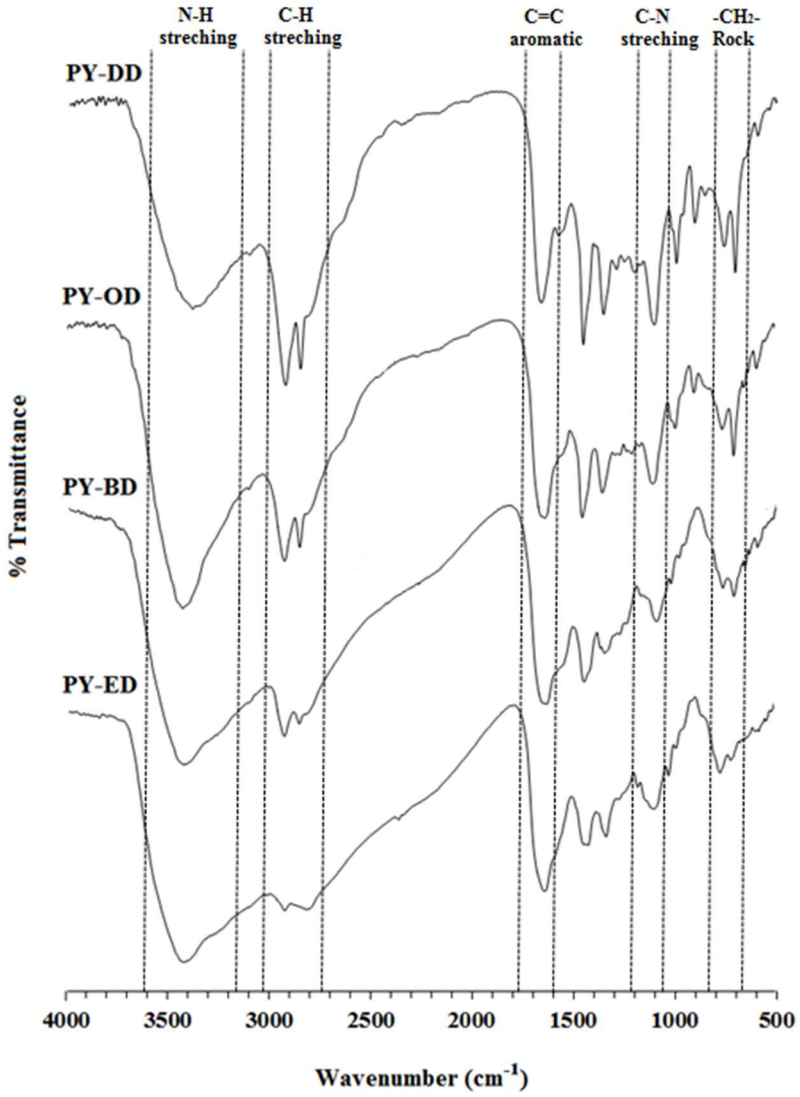


Figure 10. FT-IR spectra of cross-linked polymers.

Solid-state ^{13}C-NMR spectra were taken using Bruker WB-400 spectrometer with a spinning rate of 10 KHz. Solid-state ^{13}C-NMR spectra of the synthesized cross-linked polymers are shown in Figure 2. The assignment of peaks and spectra confirmed the proposed structure shown in the figure, a peak ~80 ppm revealed the formation of a 1,3,5-Triazinane ring in the cross-linked terpolymers. The peak ~30 ppm is assigned for the aliphatic chain which is originally from the alkanediamine. The aliphatic carbons adjacent

to the nitrogen atoms in the chain have been assigned the broad peak ~50 ppm. While the aromatic carbons from pyrrole have been assigned the peaks from ~110- 130 ppm.

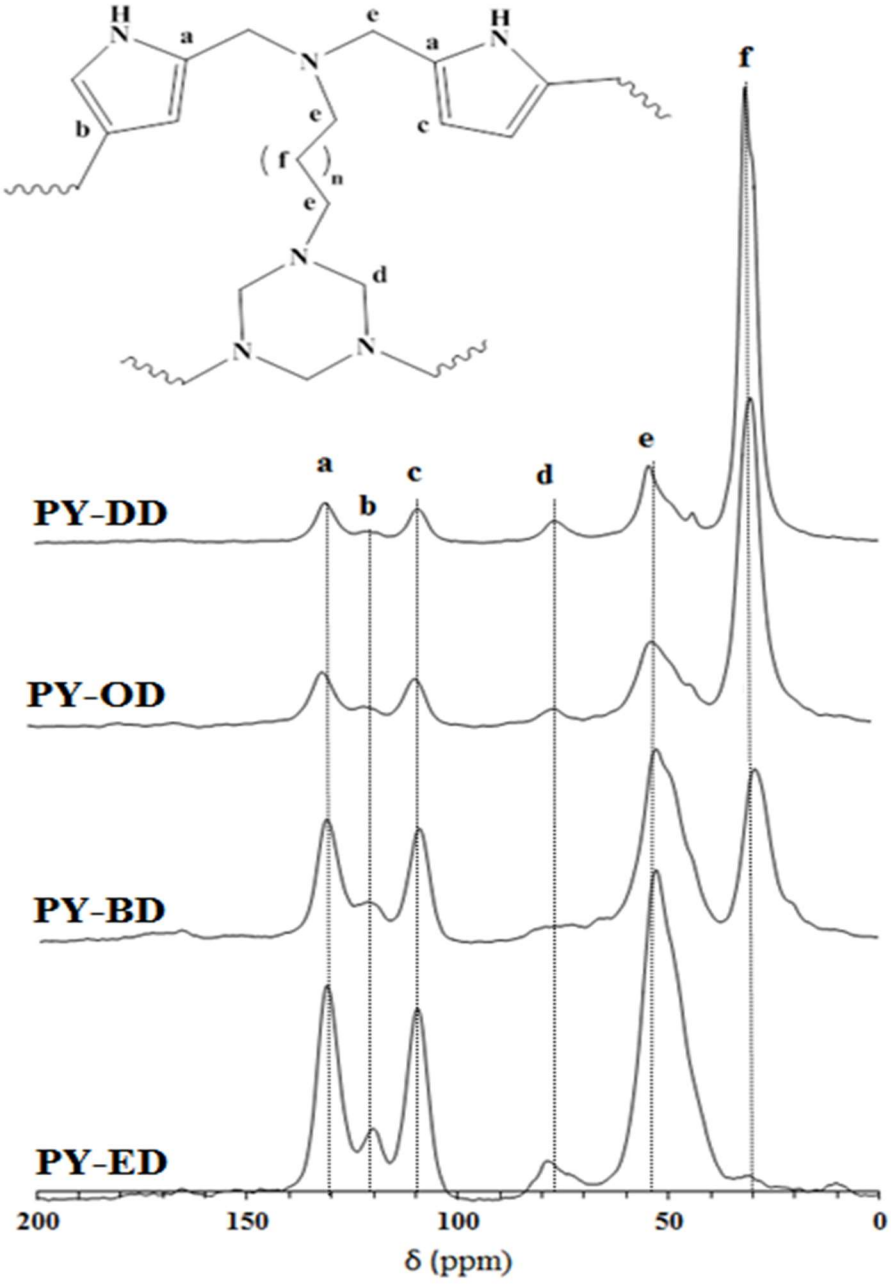


Figure 11. Solid-state ^{13}C-NMR spectra of cross-linked polymers.

TGA and DSC experiments were performed to analyze the thermal stability of the terpolymers. Thermogravimetric analysis (TGA) of the synthesized cross-linked polymers shown in figure 12 shows a trend in the thermal stability between the four terpolymers. The longer the chain length the more the thermal stability. The thermal degradation of the terpolymers starts around 190 °C.

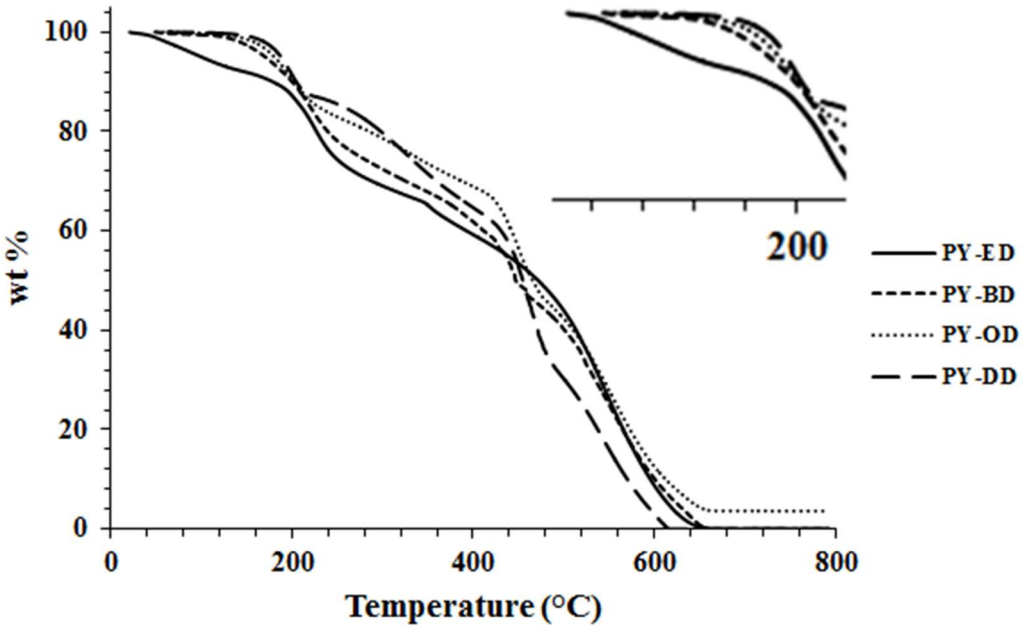


Figure 12. Thermogravimetric Analysis of cross-linked polymers.

Differential scanning calorimetry measurements were performed using NETZSCH DSC 204 F1 Phoenix calorimeter, the thermograms of the terpolymers are shown in figure 13. The confirmation of the terpolymers being highly cross-linked in nature comes from the absence of the glass transition. The thermal behavior showed that the cross-linked polymers with small chain length began to melt ~110^{o}C followed by decomposition. Whereas for the terpolymers with a longer chain, decomposition step occurs directly.

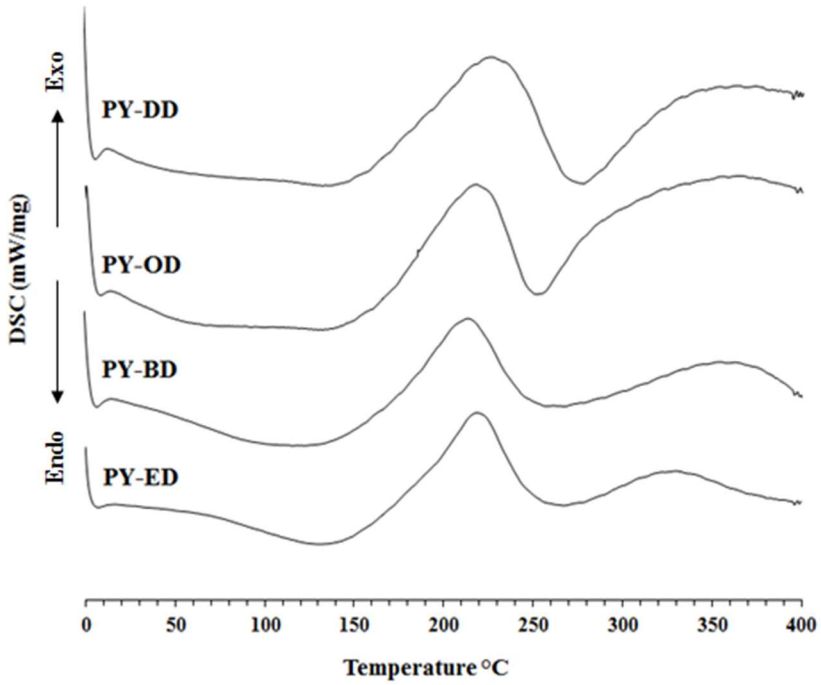


Figure 13. DSC thermograms of the cross-linked polymers.

3.3.2. Characterization of the Modified terpolymers

FT-IR and ^{13}C NMR spectra of the modified polymers are shown in figures 14 & 15 respectively.

For the FT-IR, the spectra show the presence of new bands ~ 1000 & ~600 cm^{-1} assigned for the symmetric and asymmetric C-S stretching vibrations. N-CS bond stretching vibrations were assigned the band ~1450 cm^{-1} [81].

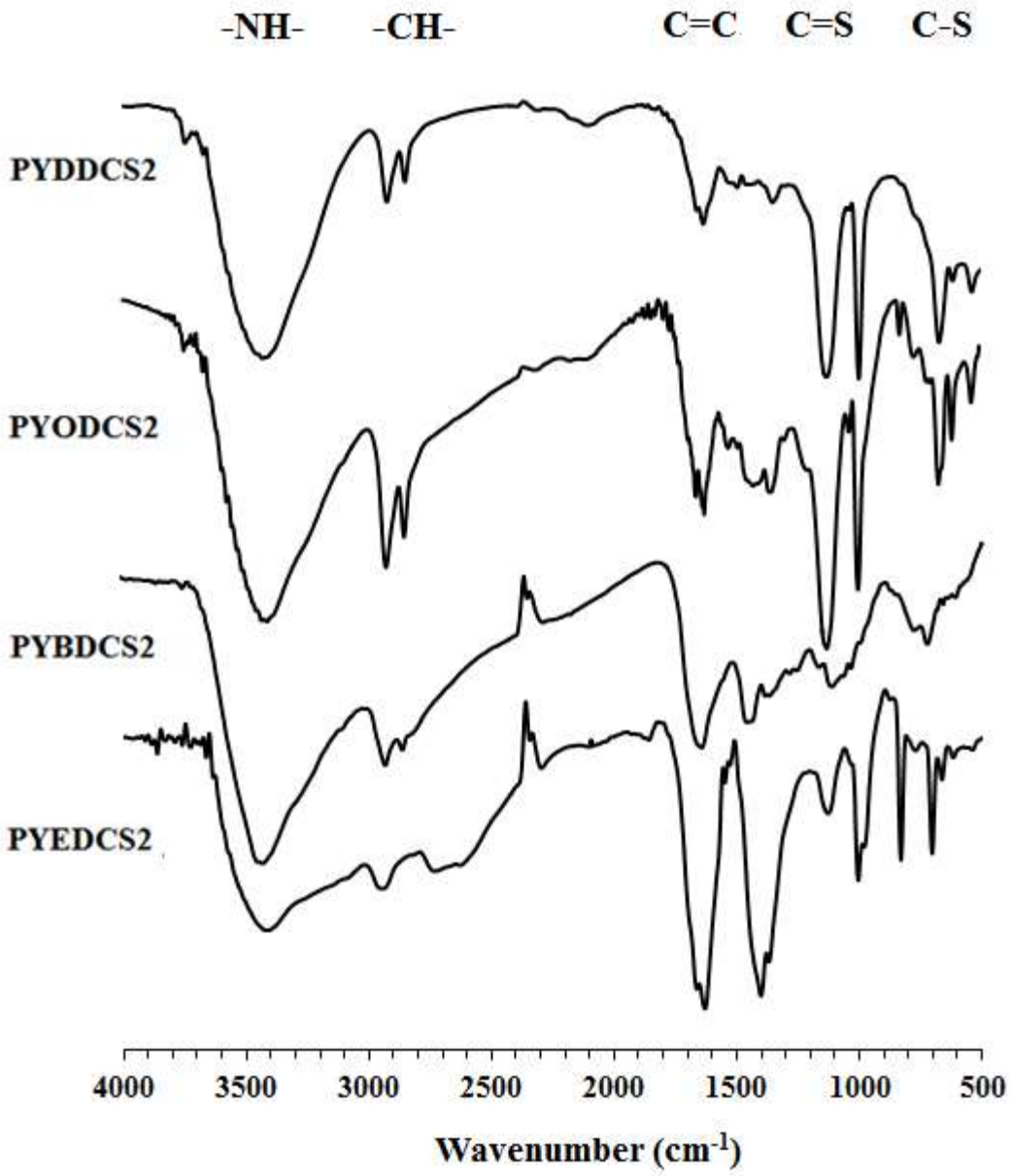


Figure 14. FT-IR spectra of the modified polymers.

^{13}C NMR spectra of the modified polymers show the appearance of the -C-S_2 peak around 208 ppm where the rest of the spectra shows a similar behavior of the original polymeric series [74].

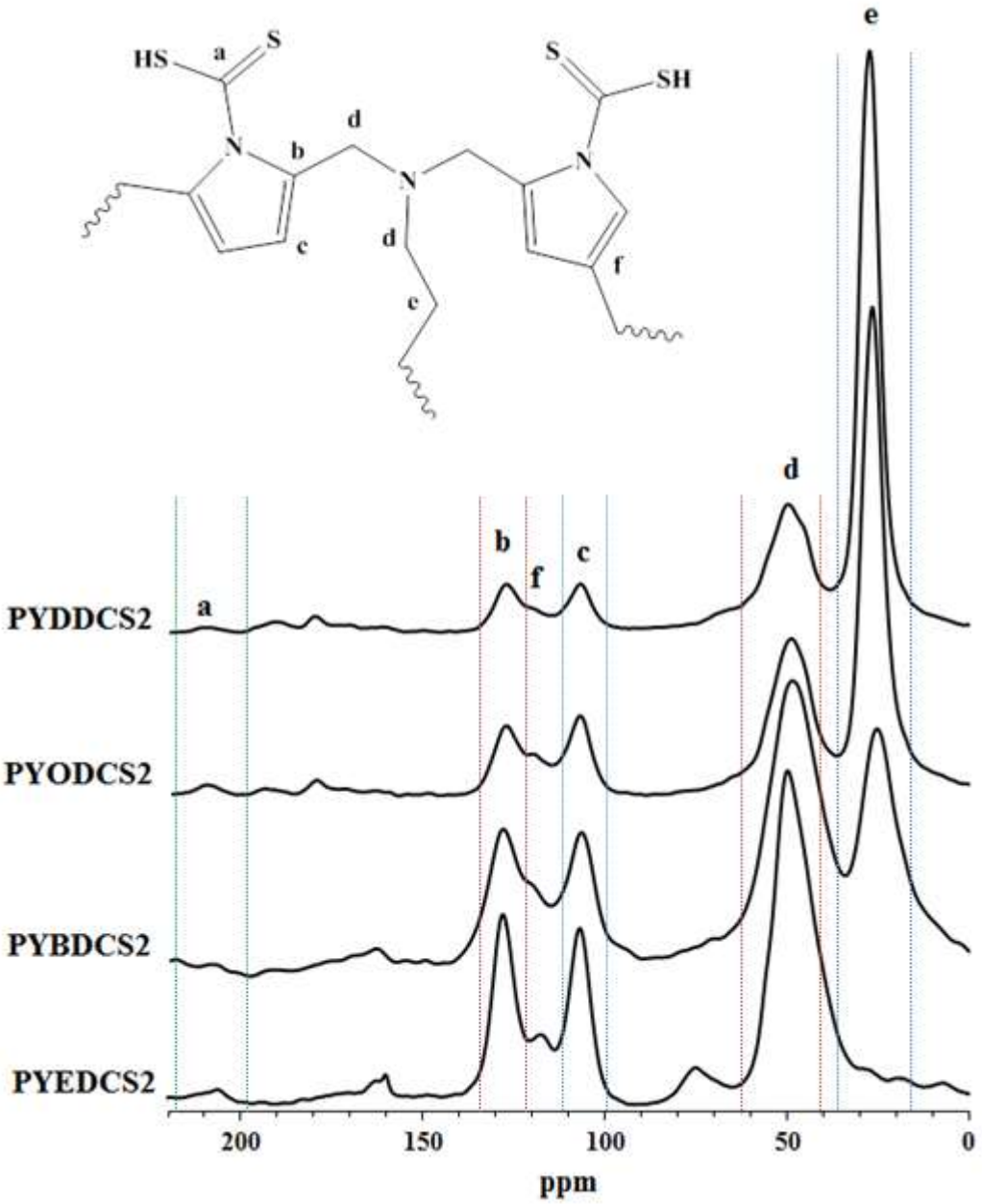


Figure 15. ^{13}C NMR spectra of the modified polymers.

Evaluation of the crystallinity of the terpolymers and their modification was performed using Powder X-ray diffraction (PXRD) spectroscopy. As expected, the polymeric series prior to modification show that these polymers are amorphous in nature as can be seen in figure 16. Remarkably, the semi-crystalline pattern has been observed in the PXRD patterns (figure 17) for the modified polymers where several well-defined peaks can be seen. Crystallinity behavior of polymers can be observed under X-Ray if their chains are closely packed in an ordered fashion. This behavior can be explained by the high chelating capability of the polymers. Chelation of potassium cations in-between dithiocarabamate moieties of the polymer chains could result in a form of chain stacking by inter-chain chelation [73]. Furthermore, it has been observed that the longer the chain the complexity of the PXRD pattern which would suggest the easiness of the longer chain to undergo inter-chain chelation which results in a higher crystallinity [82].

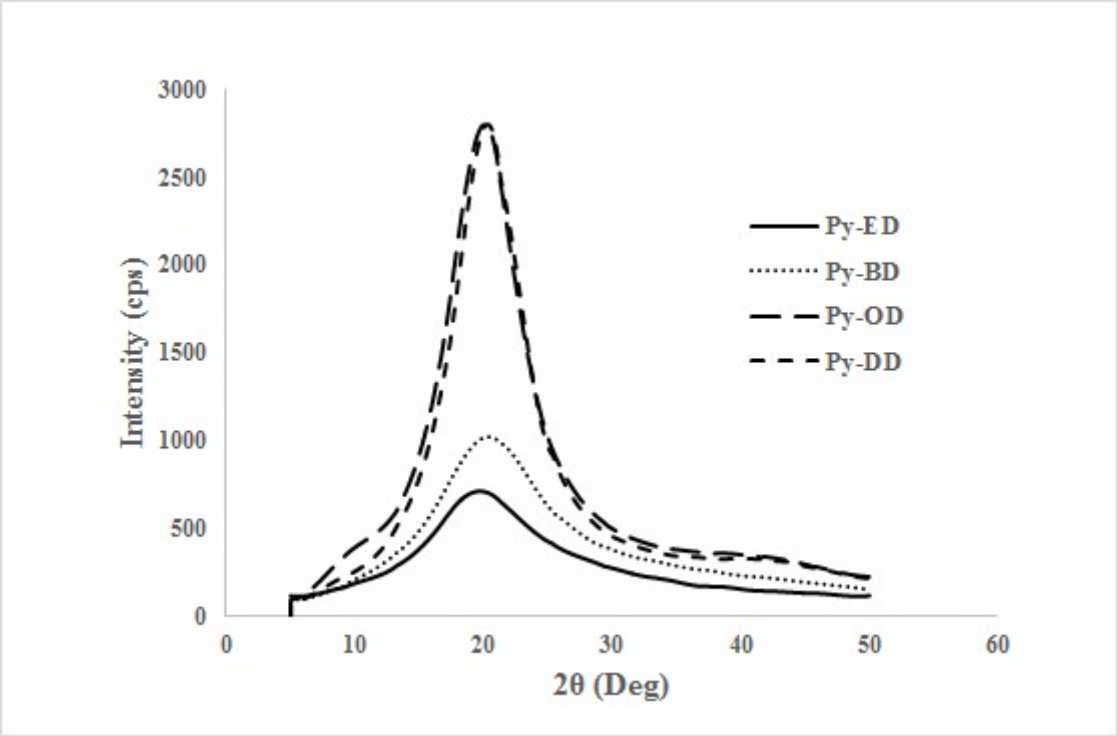


Figure 16. Powder X-ray Diffraction pattern of the polymeric series.

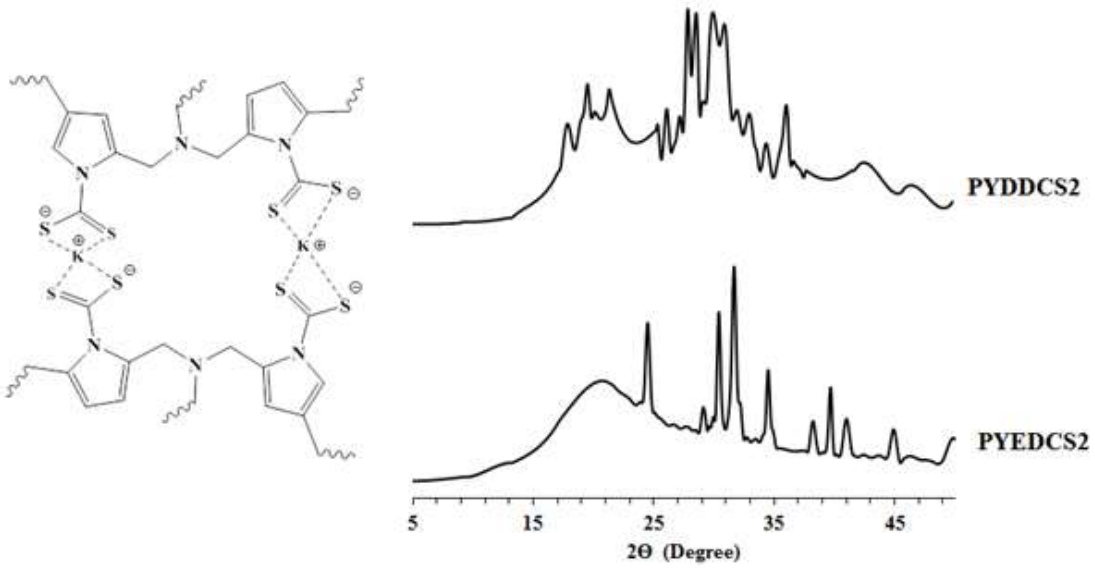


Figure 17. Powder X-ray Diffraction pattern of the modified polymeric series.

3.3.3. Adsorption properties

The Dithiocarabamate modified polymers series display an excellent attraction towards the removal of Cd^{2+} ions from aqueous solutions and wastewater samples at a concentration of 5 mg/L. This attraction can be explained by sulfur compounds' affinity to heavy metals [83]. In the case of the dithiocarbamate functionality, the presence of two sulfur atoms group would aid in the chelation of Cd^{2+} ion. Hence, the performance of Dithiocarbamate modified polymers are expected to outperform the original polyamine precursors.

3.3.3.1. Effect of Polymeric chain

The effect of the polymer chain is predicted to be primarily relied on the ratio of dithiocarbamate functionality to the hydrophilic methylene chain in the dithiocarbamate-modified polymeric series. According to the expectation, the shorter the chain length the larger the ratio of dithiocarbamate functionality which results in higher performance. This assumption was evaluated by performing Cd^{2+} adsorption experiment where ~0.03g of each polymer was stirred in 20 ml Cd^{2+} solution, 2 mg L^{-1} and for 6 hours. The bar chart in Figure 18 illustrates that the best adsorbent among the polymeric series is PYEDCS2 in the removal of Cd^{2+} ions. Therefore, PYEDCS2 was chosen for further adsorption analysis.

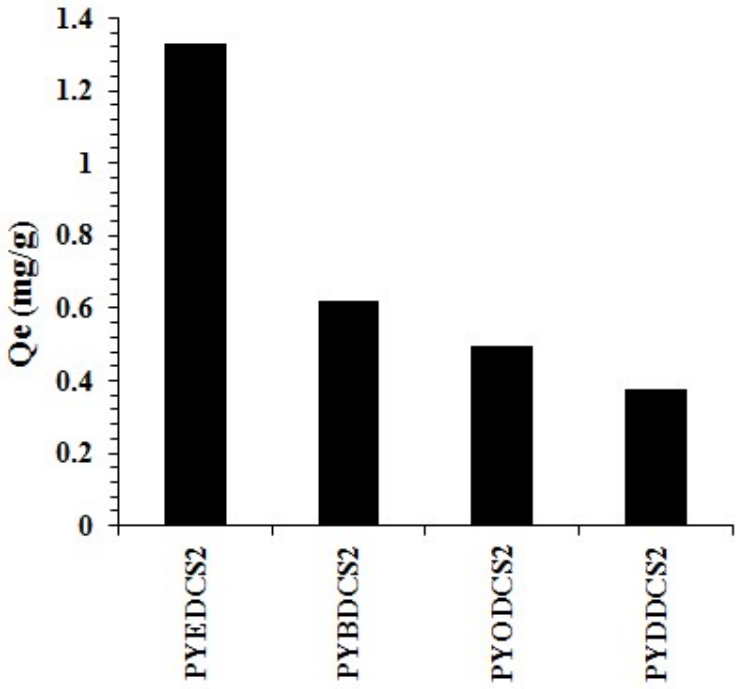


Figure 18. Preliminary adsorption performance test.

3.3.3.2. Effect of pH

The effect of pH is illustrated in figure 19. The figure shows that there is not a noteworthy effect from the pH on the metal removal performance of the polymer; which indicates that the chelation of the heavy metal ions predominates the protonation on the sulfur moieties of the polymers.

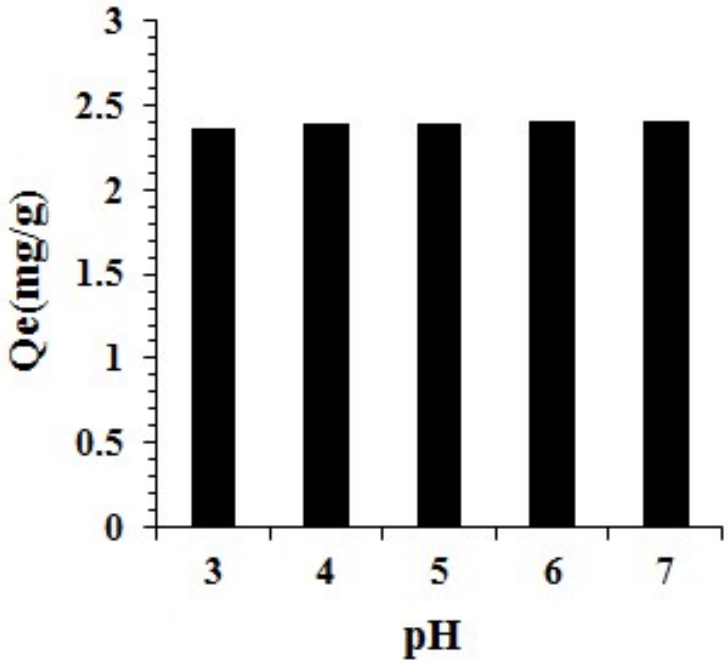


Figure 19. Effect of pH on the adsorption capacity of Cd^{2+} ions by PYEDCS2.

3.3.3.3. Effect of initial concentration and adsorption isotherms

Initial concentration effect was analyzed using Cd^{2+} ions solutions with varying the initial concentration (Co) between 1 and 5 mg L^{-1}. In figure 20a, the effect of initial concentration on the adsorption capacities of the DTC-modified terpolymers is shown. The outcomes of the test are that an increase in the adsorption capacity has been observed as the initial concentration of the Cd^{2+} solutions is increased. Langmuir and Freundlich's isotherms were applied in order to evaluate and demonstrate the adsorption mechanism.

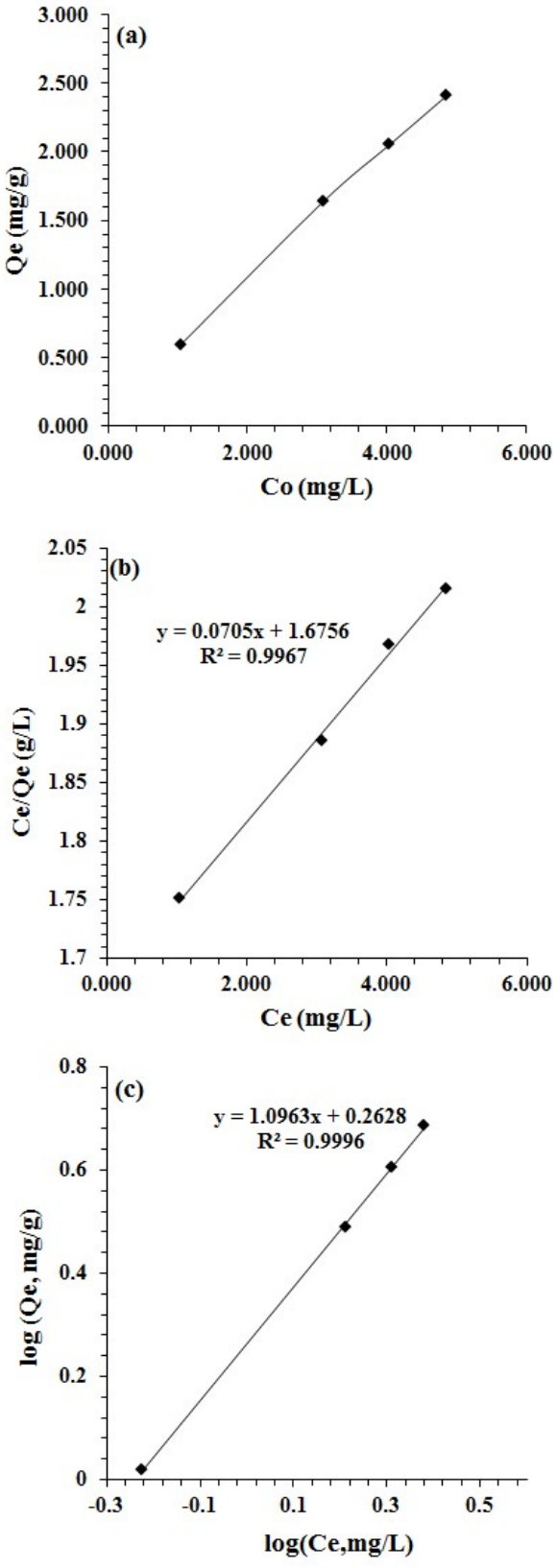


Figure 20. (a) Effect of initial concentration on the adsorption capacity of Cd^{2+} ions ions by PYEDCS2. (b) Langmuir isotherm model. (c) Freundlich isotherm model.

The Langmuir adsorption isotherm model is exploited to illustrate the homogeneity of the adsorption process of the metal ions on the surface of the adsorbent. One postulate of the Langmuir isotherm is that each metal ion is adsorbed on only one active site on the adsorbent. Langmuir isotherm can be expressed linearly by the following equation:

$$\frac{Ce}{qe} = \frac{Ce}{Qm} + \frac{1}{bQm} \qquad (2)$$

*C*e is concentration (µg L-1), *q*e is the adsorption capacity at equilibrium (µg g-1). *b* expresses Langmuir constant (L3 µg-1) where *Q*m represents the maximum adsorption capacity (µg g^{-1}). Therefore, plotting Ce/qe vs Ce yields a linear plot which its slop and intercept can be utilized to find Qm and b respectively. The linear form of Langmuir isotherm can be shown in figure 20b. based on the assumption of Langmuir isotherm, a good linear regression (R^2) value indicate that the adsorption mechanism is homogeneous on all active sites of the polymer adsorbent which they can be considered to have uniform energy [84, 85]. From the plot in figure 11b, it has been demonstrated that the adsorption process fits the Langmuir isotherm indicating a homogeneous adsorption mechanism on the surface of the polymer.

On the other hand, Freundlich isotherm expresses the adsorption on heterogeneous surfaces. The linearized form of this model can be expressed as shown in equation 3 [86, 87]:

$$log\, q_e = log\, k_F + \frac{1}{n} log C_e \qquad (3)$$

where n and k_f are Freundlich constants which their value can be obtained from the slope and the intercept respectively from the plot of the linear form of the model of log *qe* vs log *Ce* as shown in figure 20c. The values of these constants are found in table 4.

Table 4. Langmuir, Freundlich isotherm model constants for the adsorption of Cd^{2+} ions.

	Langmuir isotherm model		
Polymer	Q_m	*b*	R^2
PYEDCS2	14.184	0.042	0.9967
	Frendulich isotherm model		
	k_f	*1/n*	R^2
PYEDCS2	1.831	1.096	0.9996

3.3.3.4. Effect of Contact Time and Adsorption Kinetic Models

Temperature and contact time effects on the capacity of adsorption of the terpolymers were only analyzed on PYEDCS2 as it was concluded to have the best performance in the adsorption experiments of Cd^{2+} ions. Figure 21a illustrates the direct relation between adsorption capacity and contact time. It is a noteworthy trend that the adsorption process reaches equilibrium within 1 hour indicating efficient adsorption toward Cd^{2+} ions by PYEDCS2 which can be explained by a high electrostatic affinity between the modified polymer and the metal ion. Furthermore, as the temperature increases, it is observed that the adsorption capacity increases in addition to a slight delay in the equilibrium time. In order to find an explanation for the adsorption mechanism, Lagergren second-order kinetic model was conducted on the experimental data.

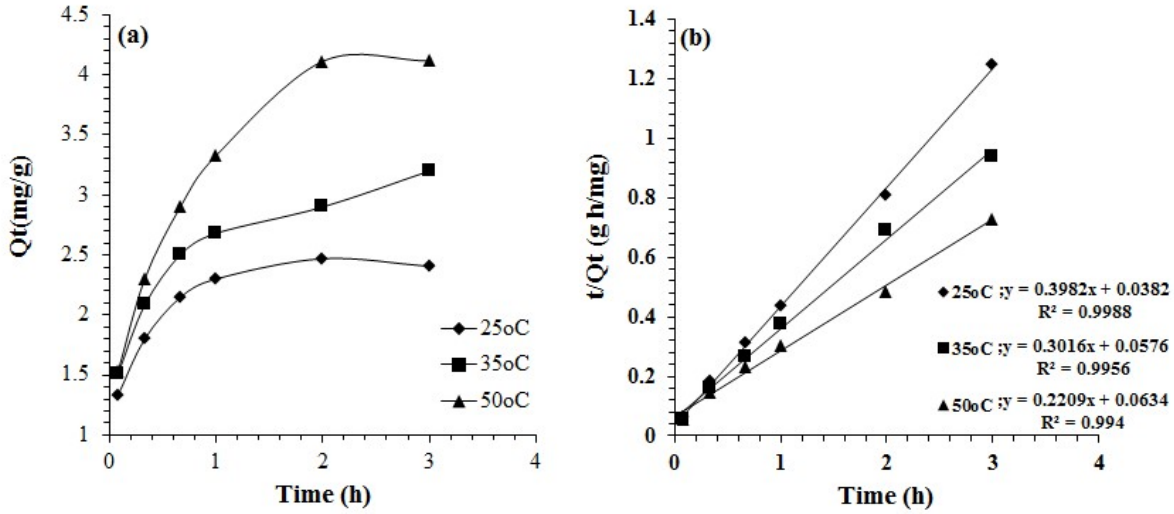


Figure 21. (a) Effect of time on the adsorption capacity of Cd^{2+} ions by PYEDCS2 (b) Lagergren second – order kinetic model.

Lagergren second-order kinetic model is used to analyze the kinetics of chemical adsorption from liquid to solid adsorbent [88]. The linear form of Lagergren second-order can be expressed in the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t (h), respectively, and k_2 (g $mg^{-1}h^{-1}$) is the rate constant for the second- order adsorption process, and $k_2 q_e^2$ (mg g^{-1} h^{-1}) or h is the initial adsorption rate.

The experimental data with high regression values fits Lagergren second-order kinetic model which assumes chemical adsorption. The good linear regression value concludes that the adsorption process depends mainly on chemisorption rather than physisorption. The increase in temperature shows increases in the adsorption capacity which may be due to the higher accessibility of Cd^{2+} ions toward the adsorption sites in PYEDCS2.

Table 5. Lagergren second–order kinetic model fitting parameters for the adsorption of Cd2+ ions[a] on PYEDCS2

			Lagergren second-order			
Metal ion	Temp (K)	$q_{e,\,exp}$ (mg g^{-1})	k_2 ($h^{-1}g\ mg^{-1}$)	h^b ($h^{-1}g^{-1}$ mg)	$q_{e,\,cal}$ (mg g^{-1})	R^2
Cd^{2+}	298	2.407	4.152	26.179	2.511	0.9988
	308	3.250	1.579	17.362	3.316	0.9956
	323	4.102	0.770	15.780	4.527	0.9940

[a]Initial metal ion concentration 5 mg/L. [b]Initial adsorption rate $h = k_2\ q_e^2$.

3.3.3.5. Effect of temperature and thermodynamics

ΔG, ΔH and ΔS of the adsorption process can be obtained by utilizing Van 't Hoff equation in its linear form as follows:

$$log(\frac{q_e}{C_e}) = -\frac{\Delta H}{2.303\ RT} + \frac{\Delta S}{2.303\ R} \qquad (5)$$

As seen in the equation ΔS and ΔH can be obtained from the intercept and slope of the graph obtained by plotting log (q_e/C_e) vs 1/T. The obtained ΔH has a positive value which indicates that the adsorption process of Cd^{2+} ions on PYEDCS2 is endothermic in nature. In addition, ΔS has a positive value which can be explained by the release of water molecules due to the breaking of the hydration bonding [86, 89]. The interaction becomes spontaneous at a higher temperature as have been observed from the decreased in the ΔG values as the temperature increases.

Table 6. Thermodynamic data and activation energy for Cd^{2+} ions adsorption on PYEDCS2

Metal ion	Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)	R^2
Cd^{2+}	298	1.715	16.99	51.27	0.9835
	308	1.458			
	323	0.433			

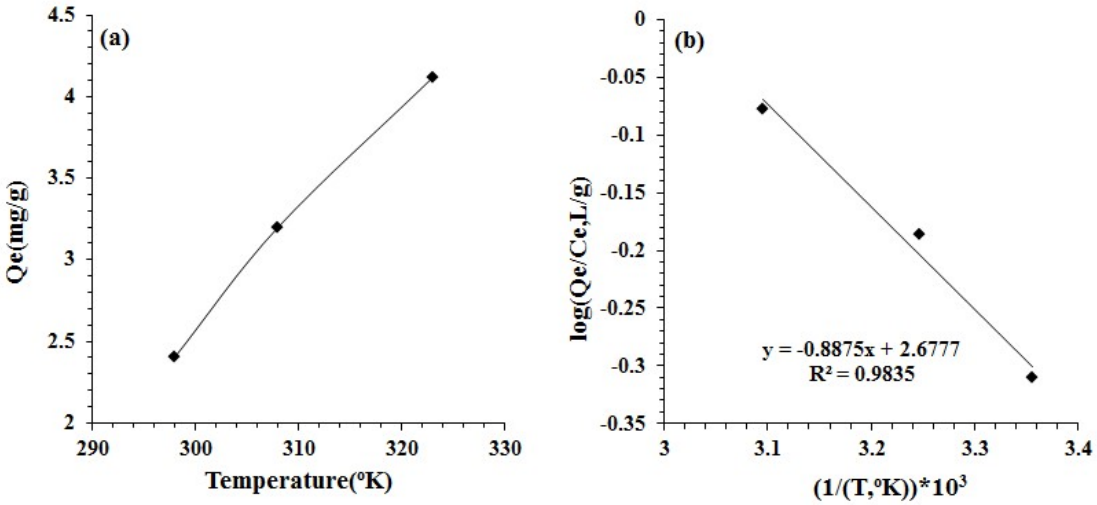


Figure 22. (a) Effect of temperature on q_e. (b) Van 't Hoff plot.

3.3.4. SEM-EDX before and after cadmium adsorption

Scanning electron microscopy images were taken by scanning electron microscopy with an energy-dispersive X-ray spectroscope (EDX) detector model X-Max was used in order to prove the adsorption of cadmium ions on the polymer. Figure 23 shows the adsorption of cadmium ions by PYEDCS2 on the surface and within the polymeric structures, from the figure

the adsorption of cadmium ions caused the polymeric particle to agglomerate around cadmium ions due to high binding affinity of the polymer toward cadmium ions.

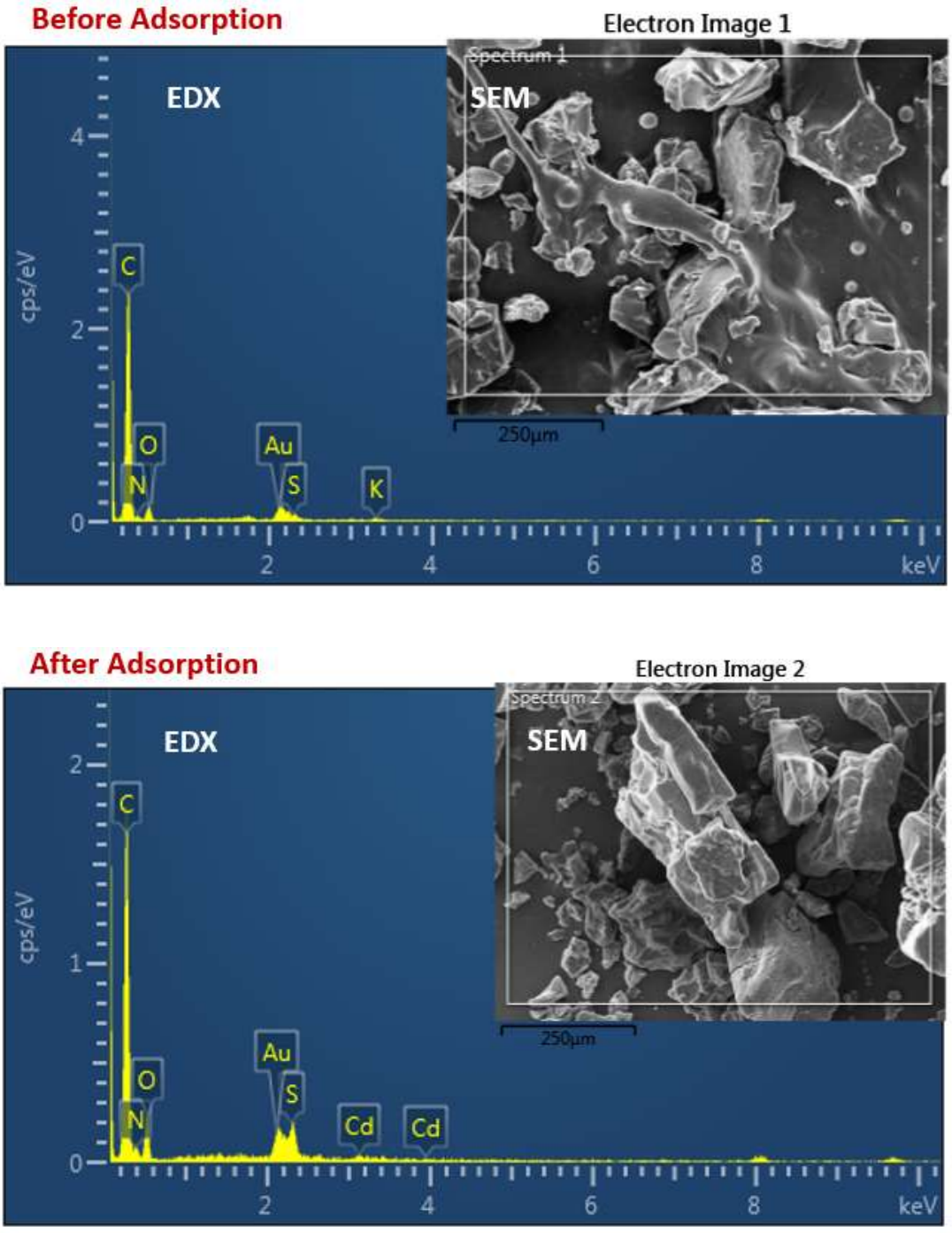


Figure 23. Before and after adsorption of cadmium ions by PYEDCS2.

3.4. Wastewater treatment

In order to evaluate the efficacy of the dithiocarbamate terpolymer, PYEDCS2 was tested on a real wastewater sample spiked with 4 mg/L Lead ions. The results revealed the efficiency of the modified terpolymer in the removal of toxic metal ions in real wastewater conditions. , PYEDCS2 efficiently removed ~ 99.7% of the spiked cadmium ions in the wastewater sample. The results prove that PYEDCS2 could be utilized as an industrial adsorbent for wastewater treatment.

Table 7. Spiked and non-spiked industrial wastewater treatment by PPYEDCS2

	Non-spiked industrial wastewater			Spiked industrial wastewater	
Metal ion	Before treatment	After treatment		before treatment	after treatment
Pb	140.9	4.375		0.493	1.356
Cd	0.238	1.018		3707	12.04
As	24.6	18.52		19.41	19.48
Zn	0	0		0	0
Cu	24.21	33.14		16.95	29.06
Ni	25.06	19.06		22.79	18.41
Co	1.591	1.017		1.496	1.118
Mn	9.677	3.124		6.558	4.672
Cr	37.66	24.39		36.07	20.4

3.5. Conclusions

The cross-linked polymer series (***Py-ED, Py-BD, Py-OD &Py-DD***) were synthesized via one-pot polycondensation reaction. The synthesized terpolymers were characterized by several techniques, and then they were subjected to modification using carbon disulfide to add the dithiocarbamate functionality. ***PYEDCS2*** cross-linked polymer showed high efficiency in the removal of cadmium ions from aqueous solution and wastewater samples.

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Publications

1. Dithiocarbamate-modified Pyrrole-based Polyamines for the Removal of Cadmium Ions. (To be submitted)
2. Lead ion removal by Novel Highly Cross-Linked Mannich Based Polymers. (Submitted)
3. A Novel Cyclopolymer Containing Residues of Essential Amino Acid Methionine: Synthesis and Application.
4. Synthesis of a Novel Zwitterionic Bisphosphonate Cyclopolymer Containing Residues of Alendronic Acid.